AN ATTEMPT TO IMPROVE THE METHODS OF ANALYSIS FOR ZINC WITH THE AID OF ORGANIC REAGENTS

THESIS for the DEGREE of Ph.D.

Presented

by

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INTRODUCTION

Zinc is a constituent of a very large number of materials and its estimation is "one of the most important of industrial analyses" (1). It may be present as a major or minor constituent, or merely in trace, and is found in association with almost any of the other elements. In view of the wide variety of circumstances in which its determination may be required, much attention has been given to methods of analysis for zinc, but many problems are found in connection with the majority of the procedures which have been described, arising from the lack of specificity of most of the reactions of zinc and the consequent difficulty in obtaining quantitative separations from other elements. While the development of spot tests (2) and of new techniques such as paper chromatography (3,4,5,6) has greatly simplified qualitative analysis for zinc, no simple, generally applicable procedure for its determination has so far been described, and the accurate determination of zinc is still, in many cases, a difficult operation.

The classical methods for the determination of zinc depend on its separation from interfering elements by refinements of the procedures normally employed in qualitative analysis (7). Metals such as lead, silver, mercury, bismuth, tin, copper, cadmium, etc. are precipitated as chlorides or as sulphides in acid solution. In the presence of copper and cadmium, great care is required to prevent loss of zinc by post-precipitation on the corresponding sulphides, and time-consuming double precipitation is frequently necessary. After the removal of such elements, zinc is commonly precipitated as the sulphide in buffered, weakly acid solution, of pH 2 to 3, in presence of

masking agents to suppress iron, nickel etc. Gallium, indium and thallium, if present, are also precipitated, and in the presence of much cobalt a second precipitation of the zinc sulphide may be necessary. While this procedure is satisfactory for the separation of zinc from most other elements, it is time-consuming, and the zinc sulphide precipitates are sometimes difficult to filter. This last point was thoroughly investigated by Fales and Ware (8), who showed that very careful control of the conditions for precipitation was necessary in order to obtain the zinc sulphide in a readily filterable form.

Some metals, e.g. aluminium, iron and lead, may be separated from zinc by precipitation of their hydroxides with ammonia, but some zinc is readily carried down and, unless the amount of other metals is small, several precipitations may be required. Most other separation techniques described for particular applications involve similar difficulties (cf. 7).

For the actual determination of the separated zinc, many procedures have been described. Gravimetric methods are considered to be most accurate (1), but in view of the thermogravimetric experiments of de Clerq and Duval (9), several must be considered unreliable as giving unsuitable weighing forms. Vance and Borup (10) have recently examined several methods by radiochemical determination of the zinc escaping precipitation.

Zinc precipitated as the sulphide has been weighed as such after heating in hydrogen, but more commonly it has been ignited to the oxide or converted into sulphate (8), which compound is not readily freed from sulphuric acid (7,11). The results of de Clerq and Duval do not support the view that zinc sulphate is formed as an intermediate during the conversion

of the sulphide into the oxide by heating in air. Tamm (12) suggested that ammonium zinc phosphate be used for the determination of zinc, as an alternative to the sulphide, and the method has since been investigated by Dakin (13) and by Luff (14). While accurate results are obtainable with care, numerous other elements, including even the alkali metals if present in large amount, interfere. Cohn (15) proposed that the complex zinc mercury(II) thiocyanate be used for determining zinc, and other workers (16,17,18) have investigated the method, which, although fairly selective, yields accurate results only with difficulty. The determination of zinc as the metal by electrodeposition has been suggested (19) and the procedure has been employed on the micro-scale (20), but correct results are not easily obtained (7).

Volumetric methods for the determination of zinc, used in conjunction with the classical separation procedures, have mostly involved the use of potassium ferrocyanide as the titrant. (21), with either a uranyl salt as an external indicator or a ferrous salt and ferricyanide as an internal indicator system (22). Potentiometric methods for the detection of the end-point (23) and, more recently, amperometric titration (24) have also been suggested. Volumetric methods depending on the precipitation of zinc mercury(II) thiocyanate have been described (17). Alkalimetric titration (25,26) and titration with sodium sulphide (7) have also been used.

Recently, the application of polarography to the determination of zinc in various types of light alloys has been reviewed (27).

One of the first applications of special organic reagents in a method for the determination of zinc was the introduction

by Cone and Cady (28) of diphenylamine and diphenylbenzidine as internal indicators in the titration with ferrocyanide, the use of which has been further investigated by Kolthoff and Pearson (29) and by Richardson and Bryson (30). Other similar indicators have recently been described (31). While these reagents improve the detection of the end-point, the separation of zinc from most other elements is still required. Many organic reagents proposed for the determination of zinc, e.g. anthranilic acid (32,33) and its 5-bromo- derivative (34), quinaldinic acid (35,36), salicylaldoxime (37,38) and ethyl oxalate (39), are applicable only after its fairly complete separation from other elements. For the detection and determination of trace amounts of zinc by colorimetric methods, much use has been made of organic reagents, particularly diphenylthiocarbazone, but they are not specific, and complicated separation procedures may be required (40,41,42).

Certain reactions involving organic reagents, which have been proposed for the determination of zinc, do, however, show considerably improved selectivity and sensitivity as compared with the classical methods. The formation of a difficultly soluble salt of zinc and 8-hydroxyquinoline was noticed by Fox in 1910 (43), but it was not until 1926 that the use of this complex for the determination of zinc was suggested (44). Its applications were investigated by Hahn and Vieweg (45) and by Berg (46,47), who showed that the reagent precipitated zinc from buffered acetic acid solutions, ammoniacal solutions, and alkaline solutions containing tartrate. Only copper^{II}, iron^{II}, magnesium and cadmium were also completely precipitated in an alkaline tartrate medium. Cobalt^{II}, indium amd titanium

could interfere by contaminating the precipitates. The selectivity of the reagent in alkaline tartrate solution has enabled it to be used on occasion without the need for a preliminary separation of zinc from other elements.

The use of ethylenediaminetetra-acetic acid (E.D.T.A.) or its salts for the volumetric determination of various metals, including zinc, has received much attention since its properties were discussed by Schwarzenbach and co-workers (48,49). With it, amounts of zinc as small as 1·5 μg have been determined (50), and many selective procedures for the determination of zinc in presence of other elements have been described, several having been published during the course of this research (51).

As well as in the determination of zinc, organic reagents have been applied in methods for its separation from other elements. Certain organic compounds, e.g. trithiocarbonic acid (52) have been suggested as substitutes for hydrogen sulphide for the precipitation of zinc as the sulphide, but the separations obtainable with them differ little from their classical counterparts. Precipitation of zinc 8-hydroxyquinolinate prior to ferrocyanide titration has been described (53), but some elements still interfere. Chromatographic methods, with paper discs (54) or strips (55), or with columns of cellulose powder (56) have been described for the separation of zinc prior to its determination in alloys.

From various published results it would seem that zinc might be separable from some other elements by the use of solvent extraction techniques. Thus cupferron (57) and acetylacetone (58) react with copper^{II}, iron^{III}, and some other elements at lower pH values than are necessary for reaction

with zinc, to form complexes which may be extracted with suitable organic solvents. Solvent extraction of nickel and cobalt as organic complexes, prior to the colorimetric determination of zinc with diphenylthiocarbazone, has been applied in the analysis of foodstuffs.(59). The theoretical basis of such extraction procedures is complicated, and some loss of zinc may occur although no complex is formed with the reagent (60).

The thiocyanates of zinc and a few other metals, e.g. copper^{II}, cobalt^{II}, manganese^{II} and cadmium, form complexes with organic bases, such as pyridine, which may be extracted into chloroform (60,61). Bock (62) studied the extraction of various metal thiocyanates with diethyl ether and the possibility of separating zinc from other elements, notably cadmium, is apparent on examination of his results. Kinnunen and Wennerstrand (63) have proposed extraction of zinc thiocyanate with methyl isobutyl ketone, in presence of masking agents to suppress copper, iron etc., as a rapid method for separating zinc from other metals prior to its determination with disodium ethylenediaminetetra-acetate. The extraction of zinc from chloride solutions into solutions of certain amines has recently been reported (64).

Prior to the commencement of this research, little use had been made of ion-exchange resins for separating zinc from other elements, but several publications relating to this topic have appeared since. The behaviour of zinc-cadmium mixtures on a cation-exchange resin had been examined, but no separation was achieved (65). The selective extraction of zinc, by means of an organic solvent from a cation-exchange resin on which cobalt and nickel were also adsorbed, had been reported (66).

Despite the large number of organic reagents which have been suggested for the determination or separation of zinc, few of these have been widely employed. The separation of zinc and cadmium by precipitation of the latter as the sulphide was being examined in 1950 (67), and the separation of zinc from some other elements by the use of activated copper has been described as recently as 1954 (68). The object of this research was to examine the application of various organic reagents to the separation and determination of zinc in small and large percentages, even if it were initially associated with many other elements, in an attempt to devise simple and reasonably rapid procedures applicable to as wide a range of materials as possible. Colorimetric and related methods used for the determination of traces were excluded from consideration and attention was concentrated on amounts of zinc ranging from about 0·5% upwards. A wide range of organic reagents has been examined although relatively few have been incorporated into the final procedures. The term 'organic reagent' has been interpreted widely (69), to include almost any organic substance or material used in connection with an analytical procedure.

It was decided to investigate primarily the application of organic reagents to the separation of zinc from other elements, as the suitability of a particular reagent for its subsequent determination would depend on what other elements were still present. After preliminary examination of a number of separation techniques, anion exchange was selected as being of most promise for further investigation. The work thereafter comprises two main sections, one dealing with the separation of 50 to 5 mg of zinc from other elements and its

gravimetric determination with 8-hydroxyquinoline, and the other with the separation of from 5 mg down to less than 500 µg of zinc and its volumetric determination with disodium ethylenediaminetetra-acetate. By these procedures, it has been found possible to determine, with reasonable precision, large and small amounts of zinc initially in association with many other elements.

APPARATUS.

Glassware Pyrex glass, which contains no zinc was used as far as possible. Special apparatus designed for particular operations will be described in the text.

Burettes, pipettes and volumetric flasks were either Grade 'A' or Grade 'B', and were calibrated when necessary by weighing the amount of water delivered or contained.

Sintered glass crucibles, filter-tubes and filter-sticks, porosity 4, were used for most gravimetric determinations. Periodic cleaning with concentrated nitric acid or with chromic acid mixture was given, after which the glassware was conditioned by thorough washing with hot, concentrated hydrochloric acid and with water.

Platinum Ware Platinum crucibles of 6 ml capacity and basins of various sizes were used in some experiments.

Plastic Ware Polythene bottles were used for storing solutions of hydrofluoric acid, ammonia, potassium cyanide, and disodium ethylenediaminetetra-acetate. Plastic tubing of various sizes was used for a variety of purposes. Polymethylmethacrylate ('Perspex') sheet was employed for the construction of special apparatus used for spectrophotometric titrations.

Balances and Weights A Towers Model 75 analytical balance, sensitive to 0·1 mg, was used for most purposes. In a few experiments, weighings to 0·01 mg were performed with an Oertling semimicro-balance. For preparation of solutions by weight, a large balance taking loads of up to 1 kg was used. The weights used were calibrated at intervals and compared with N.P.L. certified standards.

Miscellaneous A thermostatically-controlled, electrically-

heated oven was available for drying. Two simmerstat-controlled, electrically-heated hot-plates, one provided with a magnetic stirrer attachment, were used for various purposes. An electrically-driven centrifuge, capable of taking cones or tubes of from 1 to 50 ml capacity, was used to centrifuge reagent solutions and for qualitative analysis. A centrifugal pump was available for the circulation of water from thermostatically-controlled baths. A Unicam SP 500 spectrophotometer, with certain accessories to be described in the text, was used for various purposes.

By means of a steam radiator, supplemented as required by electric tubular heating controlled by a bimetallic strip thermostat and hot-wire relay switch, the temperature of the laboratory was maintained at about 17 °C while experiments were in progress.

REAGENTS

Where available, reagents of recognised analytical quality were used. Special comment is required only in the following cases.

Acids For the work with small amounts of zinc, under 5 mg. the hydrochloric and nitric acid solutions employed were prepared from AnalaR acids which had been distilled through an all-glass fractionating column.

AnalaR hydriodic acid (S.G. 1·7) was purified by treatment with hypophosphorous acid (70) and distilled in a current of carbon dioxide. Dilution, if necessary, was effected with oxygen-free water and the product was kept in an atmosphere of carbon dioxide.

Ammonia Solution Ammonia gas from a cylinder was dissolved

in water in a polythene bottle to give an approximately 5 N solution.

Chloroform The B.P. grade was washed with water, dried over calcium chloride, and distilled. The fraction boiling at 61-62°C was collected, treated with 1·5% v/v of absolute alcohol and stored in the dark. Chloroform residues from solvent extraction experiments were distilled from a water-bath and treated as above.

Disodium Methylarsonate This was prepared from AnalaR arsenious oxide by the method of Klinger and Kreutz (71). The product was dried at 160°C to the anhydrous form.

Ion-Exchange Resins Amberlite IRA-400 anion-exchange resin, 'Analytical Grade', was used in many experiments. Details of the necessary preliminary treatment will be given in the appropriate section of the text. For experiments with other resins, these were used either as supplied, or after grinding, when the material which passed a 50-mesh and was retained by a 100-mesh sieve was selected.

Pyridine Midland Tar Distillers' 'Pure' pyridine was dried over sodium hydroxide and fractionally distilled, the fraction boiling at 114-116°C being collected.

Water Distilled water from a stoneware tank fed from a stainless-steel still was used. This water was free from zinc and copper.

Miscellaneous liquid organic reagents for use as solvents, etc. were dried and distilled, suitable fractions being collected.

STANDARD SOLUTIONS

The results for zinc in most experiments relate to zinc metal as the primary standard. Hilger's H.H.P. zinc (99·99%) was used and solutions of suitable concentration were prepared by dissolving weighed amounts in hydrochloric acid. The solutions were arranged to contain that acid to a concentration of *ca.* 2 N. Large volumes, *ca.* 500 ml, of solution were prepared and distributed among several small flasks, the stoppers of which were sealed with paraffin wax to prevent evaporation. By this means, many samples could be taken from the one stock solution without significant changes in concentration due to evaporation. For experiments with 5 to 50 mg of zinc, solutions containing approximately 10 mg of zinc per ml or per gm were employed, and for experiments with smaller amounts of zinc, solutions containing about 1 mg of zinc per gm. Except in preliminary experiments with the larger amounts of zinc, where volume aliquots were taken, weight aliquots were used exclusively. These were withdrawn and transferred by means of a pre-rinsed, rapid-flow, Pyrex-glass pipette, and weighed in covered 10-ml conical flasks. In general, parallel experiments were performed with somewhat different amounts of zinc, in order to eliminate personal bias in the determinations, and frequently were related to different zinc solutions.

Solutions of known concentration of many other elements were used in the preparation of synthetic mixtures for analysis. Many of these were derived from Hilger 'Specpure' solutions, or from 'Specpure' or similar high quality solids. In general, chloride solutions, approximately 2 N in free hydrochloric acid, were employed. Control experiments were carried out when necessary in order to allow for traces of zinc in these solutions.

A PRELIMINARY STUDY OF SOME SEPARATION PROCESSES

As stated in the Introduction, it was decided to commence the research by investigating various new processes for the separation of zinc from other elements. In this section an account is given of preliminary experiments on separations by paper chromatography, solvent extraction and ion exchange.

PAPER CHROMATOGRAPHY

Although the amounts of material which can be handled on paper strip chromatograms are necessarily small, the close connection between paper chromatography and solvent extraction makes the former a useful technique for obtaining information for the development of other separation processes. Experiments were therefore carried out in order to find out what separations of zinc from other elements might be achieved, as a guide for future investigations.

Numerous solvent systems have been proposed for the paper-chromatographic separation of various elements, including zinc (3,4,5,6,55,72). One of the most striking separations in the case of zinc is obtained with the solvent system n-butanol/N-hydrochloric acid (3), by means of which it can be separated from silver, lead, copper, and the other elements, including many uncommon ones, of the analytical Groups III, IV and V. The separation from the remaining elements of Group II is less satisfactory. On examination of the separations obtainable with a number of solvent systems which had been described (cf. 72), it was found that that of zinc from cadmium was the most rarely achieved. Several solvent systems were tried in an attempt to find one which would separate zinc from the other elements of Groups II and III in a single operation.

One solvent of potential application to the zinc-cadmium separation is n-butanol/20%-hydrobromic acid (3), but on trial this was not found to be satisfactory. Similar mixtures with iodide present were examined, but no useful separations were observed. The use of thiocyanate was then considered. Martin (73) had employed a solution of thiocyanic acid in n-butanol as a chromatographic solvent. Bock (62) had studied the extraction of many metal thiocyanates with diethyl ether, and Miller (74) had used n-butyl acetate extraction of zinc thiocyanate in a scheme of qualitative analysis for separating it from nickel, manganese, scandium, titanium, zirconium and rare earths. From their results, the potentialities of employing thiocyanates for the separation of zinc from other elements were seen to be considerable.

Martin's solvent was tried: zinc travelled at the solvent front and would not therefore be separable from iron^{III}, cobalt^{II}, copper^{II}, cadmium, antimony^{III}, bismuth, mercury^{II} or silver, whose R_F values are given as 1·00. Several solvent mixtures prepared by shaking alcohols, esters etc. with acidified thiocyanate solutions were also examined, and with the majority of these, good separations of zinc and cadmium were obtained. The most satisfactory solvent for separating zinc from other elements was found to be that produced by shaking 2-ethylhexanol with an equal volume of a solution N in ammonium thiocyanate and 0·5 N in hydrochloric acid. After separation, the organic layer was employed as the developer for descending chromatograms, the atmosphere surrounding which was saturated with respect to both the organic and the aqueous phases.

With this solvent mixture, zinc, which travelled at the solvent front, was separated from the other common elements, excepting iron^{III} and tin^{IV}. Indium had an R_F value of about 0·5 but some tailing forward to the solvent front occurred. Most other elements showed R_F values of less than 0·25: many, e.g. silver, cadmium and aluminium, were virtually unmoved. Considerable backward tailing occurred, however, with zinc and the other elements which were moved with this solvent system, and while good qualitative separations of zinc from many other elements were obtained, there was little prospect of a quantitative method being developed. Further, the solvent was too viscous for consideration for cellulose column chromatography. The possibilities of the use of thiocyanates were, however, kept in mind, and at various stages in the research the obvious differences between the complexes of zinc and other metals, in particular cadmium, were further examined.

SOLVENT EXTRACTION

While the quantities of material which can be conveniently dealt with on paper-strip chromatograms are small, with simple solvent extraction operations, almost any quantity of material may be used. It was decided to relate the scale of operations in extraction experiments to the determination of up to 50 mg of zinc in samples containing *ca.* 100 mg of total metals. From examination of published compositions of various zinc-containing materials, it was found that copper, aluminium, magnesium, tin, lead and cadmium were likely major constituents, nickel and manganese might occur up to *ca.* 30% and many other elements, including several less common metals, e.g. titanium, zirconium, thorium, uranium, indium, gallium and tungsten, in

small amount, up to, say, 5%. However, any separation process should be able to cope with possible future developments, and larger amounts of some elements than are obviously necessary have often been examined, to find out what, if any, effect was produced. As useful paper-chromatographic separations had been achieved with chlorides and thiocyanates, the extraction of the corresponding zinc complexes with organic solvents was investigated as a possible separation technique.

THE EXTRACTION OF ZINC AS CHLORIDE

The direct extraction of zinc from a N-hydrochloric acid solution by shaking with n-butanol was not found to be very effective, and in a continuous extraction experiment where 10 ml of a N-hydrochloric acid solution containing 10 mg of zinc and 5 mg of each of copper^{II}, iron^{III}, and titanium^{IV} was extracted overnight with n-butanol, these other elements, which move only slightly on paper chromatograms, were found to be significantly extracted. Many other organic solvents were examined as extractants for zinc chloride from neutral and acid solution, but in no case was the degree of extraction sufficient to merit further investigation. The best extractants were ketones, e.g. cyclo-hexanone and methyl ethyl ketone, but only ca. 25% of 100 mg of zinc was extracted by 5 ml of the first named from 10 ml of a N-hydrochloric acid solution. The recently reported extraction of zinc from hydrochloric acid solutions with solutions of methyl di-octyl-amine or tribenzyl-amine in organic solvents (64) has not been examined.

THE EXTRACTION OF ZINC AS THIOCYANATE

From the data given by Bock (62) for the extraction of metal thiocyanates with diethyl ether, it seemed probable that

zinc could be separated from many other elements, e.g. cadmium, arsenic, antimony, bismuth, nickel etc. by solvent extraction as the thiocyanate. In qualitative analysis, Miller (74) had employed n-butyl acetate for extracting zinc thiocyanate in order to separate it from several other elements. Johnson and Johnson (75) proposed extraction of zinc thiocyanate with ether from slightly acid solutions of low thiocyanate concentration for the detection of zinc in cobalt salts. Since it is more easily handled than ether, yet functions similarly, it was decided to examine the use of n-butyl acetate as an extractant for zinc thiocyanate in quantitative analysis. Experiments were carried out along the lines indicated by Bock for studying the extraction with ether, in order to select conditions suitable for the quantitative extraction of zinc, and then the behaviour of some other elements was examined in order to find out whether the method would merit detailed examination as a separation technique.

The Effect of varying Conditions on the Extraction of Zinc — Most experiments were performed with neutral or hydrochloric acid solutions, but in a few, chlorides were deliberately excluded, in case some extraction of chloride was occurring, and sulphuric acid was used instead of hydrochloric acid. In general, equal volumes of the desired aqueous phase and anhydrous n-butyl acetate were mixed and stirred for an hour in a flask in a thermostatically-controlled water-bath at a selected temperature, the phases were then separated, and the zinc in suitable aliquots determined by conversion into sulphate and titration with ferrocyanide. Except in a few experiments with high thiocyanate concentrations in the initial aqueous solutions,

no significant change in the relative volumes of the phases was observed.

In both neutral and 0·5 N-hydrochloric acid solutions, the extraction of zinc thiocyanate was found to become less complete with increase in temperature; all later experiments were therefore performed in ice-water baths at approximately 0°C. The extraction was throughout more efficient from neutral than from acid solutions, as evidenced by the following results for extraction from solutions M in potassium thiocyanate by an equal volume of n-butyl acetate, the initial zinc concentration being ca. 0·05 M.

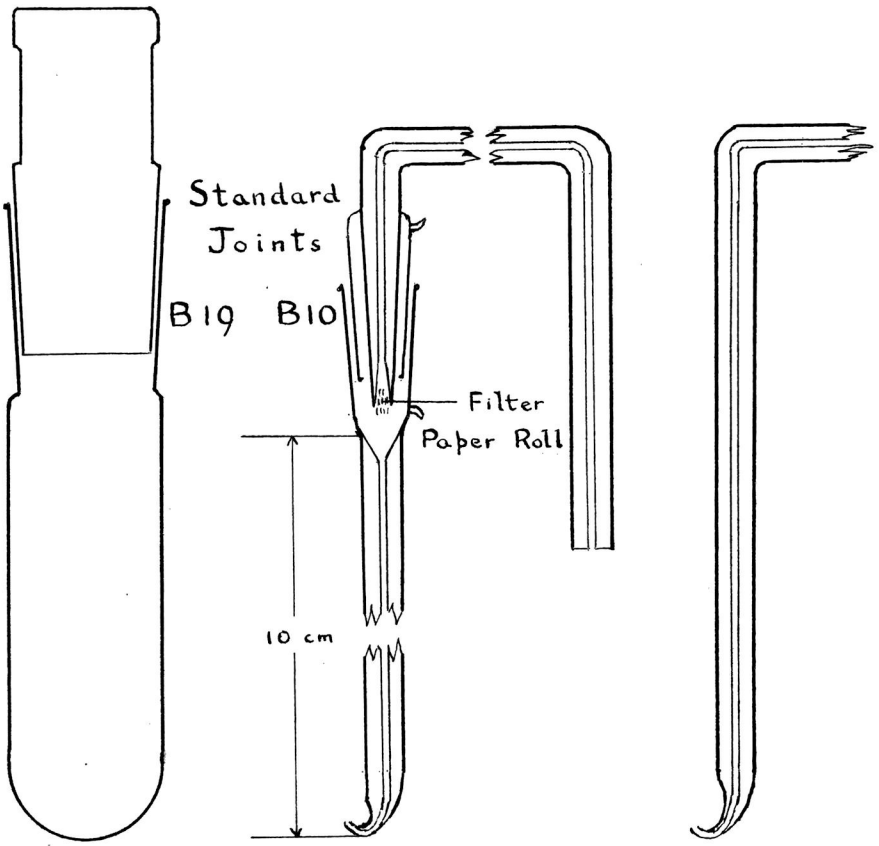
Normality of HCl	0	0	0	0·5	0·5	0·5
Temperature, °C	0	20	40	0	20	40
Zinc extracted, %	92	87	51	90	80	46

As might be expected from Bock's data, increase in the concentration of thiocyanate improved the extraction until a concentration of ca. 1 M was reached, after which relatively little effect was observed, especially with neutral solutions. The results below were obtained in experiments with various concentrations of potassium thiocyanate in neutral and 0·5N-hydrochloric acid solutions at 0°C.

Acidity, HCl, N	0	0	0	0	0·5	0·5
Molarity of KCNS	0	0·4	1	2	1	5
Zinc extracted, %	0	70	95	95	90	99

Substitution of N-sulphuric acid for 0·5 N- hydrochloric acid did not significantly affect the results. It is seen that even in 0·5 N- hydrochloric acid solutions, almost complete extraction can be attained.

It was decided that extraction from a 0·5 N-hydrochloric acid solution, M in potassium thiocyanate, at a temperature of



FULL SIZE

FIGURE 1

0°C would be employed in quantitative experiments, for, while increase in the concentration of thiocyanate might slightly increase the degree of extraction of zinc, the extraction of other elements, e.g. cobalt and beryllium, would also be increased if Bock's findings applied to butyl acetate extraction. While neutral solutions would have given better extraction of zinc, many elements would hydrolyse and precipitate unless a complexing agent such as tartrate were added, which might itself hinder the extraction of the zinc. As a 100 mg sample of a zinc-containing material would generally be readily convertible by suitable treatment into 10 ml of a 0·5 N-hydrochloric acid solution, this volume of aqueous phase was selected. The finally adopted procedure for the extraction of zinc thiocyanate was as follows.

To 10 ml of an approximately 0·5 N-hydrochloric acid solution containing 5 to 50 mg of zinc, contained in a stoppered tube (Fig. 1a), add 1 g of solid potassium thiocyanate, shake to dissolve and cool thoroughly in ice-water. Add 5 ml of cooled n-butyl acetate and shake the tube vigorously for one minute, holding it in the vicinity of the stopper in order to minimise heating by the hand. Replace in the cooling bath and allow the phases to separate, or alternatively centrifuge and cool again. Withdraw as much of the organic layer as possible by suction through a bent capillary with an upward-pointing tip (Fig. 1b), collecting it in a suitable vessel. The small roll of filter-paper serves to remove any entrained droplets of the aqueous phase. Repeat the extraction with four fresh portions of the ester, added in such a manner as to rinse the ground surface of the stopper seating as thoroughly as possible.

The Determination of the extracted Zinc — In preliminary experiments, the zinc contained in the ester was determined by evaporation, destruction of the thiocyanate by means of nitric acid, conversion of the residue into sulphate and titration with ferrocyanide. Since it was obvious that, in dealing with mixtures, other elements, e.g. iron^{III}, would be liable to be extracted and to interfere in this method for the determination of the zinc, a more selective procedure was required. The precipitation with 8-hydroxyquinoline in an alkaline tartrate solution (46) is one of the more selective procedures for determining zinc, and its application to the butyl acetate extracts was therefore examined. It was found that zinc could be quantitatively extracted from the ester into a sodium hydroxide solution containing tartrate, and that, after elimination of the dissolved ester by extraction with ether and heating to expel traces of the latter, the zinc could be precipitated with 8-hydroxyquinoline. The results obtained lacked precision, which was probably due to the uncertainty associated with the precipitation technique, which was not thoroughly investigated until later (see p. 34 et seq.), but they indicated that extraction and recovery of 10- and 50-mg amounts of zinc were essentially complete, within, say, 0·2 mg. The procedure for the extraction of the zinc from the ester was as follows.

To the ester solution of zinc thiocyanate in a stoppered flask add 25 ml of a solution containing 75 g of tartaric acid and 60 g of sodium hydroxide per litre. Stir (magnetic stirrer) or shake vigorously for a few minutes. Allow to settle and withdraw the ester layer through a bent capillary with upward pointing tip (Fig. 1c, p. 19*). Wash the ester with a few ml of water, allow to settle, withdraw and discard the ester layer

and add the water extract to the alkaline tartrate solution. Extract this with 5 ml of ether, withdraw carefully and discard the ether layer. Heat the aqueous solution on a steam-bath until the ether is expelled, adding more alkali if required to dissolve any precipitate. Cool and precipitate with 8-hydroxyquinoline as described on p. 39.

The Behaviour of Other Elements — Since n-butyl acetate and diethyl ether behaved similarly as extractants for zinc thiocyanate, it seemed probable from Bock's data that the following would not be extracted to any appreciable extent: copper^{I}, cadmium, mercury^{II}, germanium, arsenic^{III}, arsenic^{V}, antimony^{III}, bismuth, chromium^{III}, nickel, and aluminium. Cadmium was shown experimentally not to be extracted. Elements predicted or found to extract in significant amount were copper^{II}, iron^{III}, tin^{IV}, cobalt^{II}, gold^{III}, uranium^{VI}, titanium^{IV}, indium, gallium and scandium. Thus of 50 mg of indium, titanium and uranium, 100, 15 and 80% respectively were extracted by the procedure described on p.19. The elements underlined in the above list were known to interfere in the determination of zinc with 8-hydroxyquinoline in alkaline tartrate solution. The extraction of copper, in particular, was examined, as the method would be really useful only if interference due to it could be prevented, although masking with cyanide might be employed to prevent its precipitation with 8-hydroxyquinoline (76).

On addition of thiocyanate to a solution of copper^{II}, the resulting black copper (II) thiocyanate which precipitated out was found to be partially dissolved on shaking with n-butyl acetate, and the undissolved solid collected at the phase

boundary, even after centrifugation, and made satisfactory separation of the layers impossible. Reduction by means of sulphur dioxide did not help, as the precipitate of copper (I) thiocyanate which then formed likewise collected at the interface. Removal of the precipitates by filtration or centrifugation was not considered desirable as the necessary modifications in the procedure, required in order to obtain a satisfactory separation, might be troublesome. Various unsuccessful attempts were made to eliminate copper by extraction as an organic complex, e.g. with acetylacetone, cupferron, α-benzoin oxime or quinoline and iodide, either before the addition of thiocyanate or after the back-extraction into the alkaline tartrate solution.

(Some time later, on the appearance of the paper by Kinmunen and Wennerstrand (63), the masking of copper with thiourea as described therein was tried, but, possibly because of the high concentration of copper under consideration, some precipitate was found to form on addition of thiocyanate to a solution containing copper and thiourea. Further, the presence of thiourea caused extraction of cadmium, which was not extracted in its absence. As the separation of zinc from other metals by anion exchange (see p. 42 et seq.) had been developed by that time, no detailed investigation was carried out.)

Some study was also made of the separation from zinc of the cobalt^{II}, *ca.* 10 mg from 100 mg taken, extracted along with it. It was found that on passage of the ester extracts through a column of silica gel, moistened with a solution M in thiocyanate and 0·5 N in hydrochloric acid, and packed in *n*-butyl acetate, the zinc, and any copper^{II} or iron^{III} present passed

through, whereas the cobalt was held as a blue-purple band at the top of the column. While this was of interest as an example of true partition chromatography applied in inorganic analysis, the procedure suffered from the disadvantage that only one sample of silica gel, from a number which were examined, gave satisfactory columns, and even this sample would require preliminary purification if the zinc were to be determined by a procedure in which iron^{III} would interfere, as much iron was liberated from the silica.

While zinc could be quantitatively extracted as thiocyanate with n-butyl acetate and determined subsequently with 8-hydroxyquinoline, the method was only of limited application because of the extraction of other elements, e.g. copper, likely to be present along with it in materials and liable to interfere in its determination. The extraction was of interest as a means for separating zinc and cadmium, and might be applicable in the analysis of some materials containing none of the other extractable and interfering elements, but in view of the desire for a generally applicable separation technique for use prior to the determination of zinc, attention was transferred to other separation processes.

ION EXCHANGE

Since neither paper chromatography nor solvent extraction had yielded a fully satisfactory method for separating zinc from other metals, the possibility of achieving adequate separations by ion exchange was examined. In view of the separations already obtained in presence of thiocyanate, some experiments were carried out, with cation- and anion-exchange resins, on solutions of zinc and other metals, e.g. iron^{III} and cobalt^{II}, containing that ion, but no useful separations were detected. The publication by Kraus and Moore of their "Anion Exchange Study of the Transition Elements, Manganese to Zinc" (77) made apparent the possibility of separating zinc from manganese^{II}, iron$^{II \text{ and } III}$, cobalt^{II}, nickel and copper^{II} by anion exchange with hydrochloric acid solutions. A number of small-scale experiments were performed in order to obtain information about the behaviour of other elements, particularly those which would interfere in the determination of zinc with 8-hydroxyquinoline in alkaline tartrate solution.

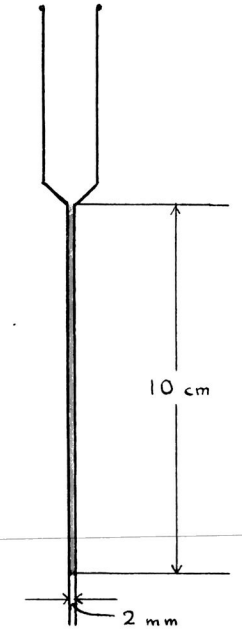


FIG. 2
(half actual size)

Dowex-1, the resin used by Kraus and Moore, was not readily available, and the comparable material, Amberlite IRA-400 (Analytical Grade) was used. Columns (10 cm long x 2 mm diam.) of this resin (150 to 200 mesh) in the chloride form were prepared by packing as a slurry in 2 N hydrochloric acid into Pyrex glass tubes (Fig. 2) filled with that acid. The resin was supported on and retained by small plugs of

cotton wool, the upper of which served to prevent the columns from running dry. 0·1 Ml of 2 N-hydrochloric acid solutions of various metal ions were applied and the columns washed with 2·5 ml of that acid, in order to remove non-adsorbed ions. Zinc and certain other elements were held by the resin. On changing the washing liquid to water, zinc and some other elements were eluted. The results for various ions are given in Table I. The effluents were examined by collecting suitable fractions on spot-plates and applying appropriate spot tests.

TABLE I

Ion	Amount, mg	Behaviour in 2 N-HCl	Behaviour with water	Separable from zinc
Zn	1-5	H	(E)	-
Cd	1	H	(E)	no
Cu^{II}	2	(E)	trace	mostly
Fe^{III}	2	E	-	yes
In	1	Part H	(E), slow	unlikely
Ti^{IV}	1	E	-	yes
U^{VI}	1	E	-	yes
Bi	1	H	H*	yes
Hg^{II}	2	H	H	yes
Be	0·2	E	-	yes

E = eluted, E = rapidly eluted, (E) = eluted with long tail

H = held, H* = held because of hydrolysis.

5 Mg of sulphate, nitrate, phosphate, arsenate and molybdate were not apparently held by the resin, and did not interfere with the adsorption of 1 mg of zinc from 2 N-hydrochloric acid solution nor with its subsequent elution by water.

In similar small-scale experiments, the separation of zinc

from copper^{II} and iron^{III}, and from bismuth was found to occur according to prediction. The zinc and bismuth were adsorbed by the resin from the 2 N-hydrochloric acid solution and the zinc alone was eluted by water.

From these results and from Kraus and Moore's data, it seemed probable that zinc could be separated from copper^{II}, iron^{III}, titanium^{IV}, uranium^{VI}, bismuth , mercury^{II}, beryllium, cobalt^{II}, nickel and manganese^{II}. Other metals, e.g. magnesium and aluminium would probably also be separable. It was therefore obvious that, of the separation techniques so far examined, anion-exchange adsorption of zinc from chloride solutions was the most likely to lead finally to a generally applicable procedure. When used in conjunction with the precipitation of zinc with 8-hydroxyquinoline from an alkaline tartrate solution for the final determination of the zinc, serious interference would be expected only from cadmium and indium, with perhaps traces of copper, and cadmium might be dealt with by a subsequent solvent extraction with thiocyanate. At the time, 8-hydroxyquinoline was considered the most suitable reagent for the determination of zinc after anion-exchange separations, as with its aid traces of many elements, which might not be completely separated, could be rendered non-interfering. Some other reagents, e.g. potassium mercury (II) thiocyanate (18), 5-bromoanthranilic acid (34) were considered and a few experiments were performed, but their selectivity was obviously inferior to that of 8-hydroxyquinoline in an alkaline tartrate solution.

For quantitative examination of the method, it was decided to deal with the same quantities as had been considered in relation to solvent extraction (p.15), namely up to 50 mg of

zinc in association with 100 mg of total metals, as might be obtained from a 100 mg sample of an alloy or, say, a 150 mg sample of an ore. Initially, a lower limit of 5 mg of zinc was set for most experiments where 8-hydroxyquinoline was employed for the determination of the zinc. The use of 8-hydroxyquinoline for the determination of zinc and of anion exchange for its separation from other elements prior to such determination was now more closely examined.

(During the course of the subsequent researches, several papers relating to ion-exchange separations of zinc from other elements were published. These described the use of cation exchange for separating most of a large amount of magnesium before determining zinc with disodium ethylenediaminetetra-acetate (78), the separation of zinc, copper, cobalt and gallium by anion exchange in presence of bromide (79), the use of anion exchange for the separation of small amounts of zinc from other elements, initially in chloride solution, prior to its colorimetric determination (42), the separation of zinc and cadmium by anion exchange in presence of iodide (80) and the separation of gallium, germanium and indium from other metals, including zinc, by cation exchange (81). Papers describing the anion-exchange behaviour of additional elements in chloride solution have been published by Kraus and co-workers (82,83) whose results confirm those obtained in this research.)

(A paper on the anion-exchange behaviour of various elements, including zinc, in hydrochloric acid solutions has just been published in Germany (83*)).

THE DETERMINATION OF ZINC WITH 8-HYDROXYQUINOLINE

While 8-hydroxyquinoline precipitates zinc in buffered acetic acid, ammoniacal and alkaline tartrate solutions (46), the first- and last-named conditions have been most frequently employed. For the completion of the determination after the precipitation, various methods have been proposed. The precipitate may be filtered and weighed after suitable drying (46); or dissolved in acid and the liberated 8-hydroxyquinoline determined by titration with a standard bromate solution (46,76); or the zinc may be determined by ferrocyanide titration after the destruction of the organic part of the precipitate (53). In this research, weighing of the zinc 8-hydroxyquinolinate was chosen for the determination, as by this means subsequent testing of the precipitates for contamination by foreign metals would be most easily performed. In view of the finding of Chirnside and co-workers (84) that at 160°C the anhydrous complex became crystalline, this drying temperature was used for all experiments. It is well within the range of temperature for stability of the anhydrous form, given by de Clerq and Duval (9) as 127 - 284°C. Precipitates dried at 160°C were found not to be hygroscopic, and no special precautions were therefore necessary during cooling and weighing.

Precipitations in buffered acetic acid and in alkaline tartrate media were examined, and Berg's methods adapted as required in order to give reasonably reliable procedures for the determination of zinc in solutions such as might be obtained from ion-exchange experiments.

PRECIPITATION IN BUFFERED ACETIC ACID SOLUTION

In solutions buffered at pH ~5 with acetic acid and an acetate, zinc can be separated from small amounts of lead, magnesium and manganese, whose 8-hydroxyquinoline complexes begin to form only at somewhat higher pH values, as well as from the alkali and alkaline earth metals (47). Zinc cannot be separated thus from copper, iron, cobalt, nickel, bismuth, cadmium, etc. The method would therefore be applicable only if such interfering elements were absent, or their removal by ion exchange were essentially complete.

The following procedure, relating to the determination of 5 to 50 mg of zinc, in solutions such as might be obtained from anion-exchange columns about 15 times larger than those used in the preliminary experiments, was deduced from those proposed by Berg and used as a basis for further experiments.

To the solution, of volume *ca.* 60 ml and containing *ca.* 5 ml of 2 N-hydrochloric acid, add 5 N-ammonium hydroxide until neutral to methyl red, followed by 0·1 ml of glacial acetic acid and 6 ml of 30% w/v ammonium acetate solution. Heat to about 60°C and precipitate the zinc by the gradual addition of an excess of a 2% w/v solution of 8-hydroxyquinoline in 0·8 N-acetic acid. Heat gradually to boiling and after maintaining that temperature for a few minutes, allow to cool slightly and filter. Transfer and wash the precipitate with the minimum volume of hot water and dry at 160°C to constant weight.

In a trial experiment on the precipitation of 50 mg of zinc, with a slight excess of 8-hydroxyquinoline, the pH of the solution fell during the precipitation from 6·1 to 4·8. This latter figure is safely above the minimum pH for complete formation of zinc 8-hydroxyquinolinate, which, according to

Berg (47), is 4·6, and according to Borrel and Pâris (85), 4·5. A number of experiments with ca. 50 mg of zinc were carried out by procedures differing slightly from that given above. The results are given in Table II (p.31). In some cases the filter crucible was weighed after dissolving out the precipitate, but no loss in weight during an experiment was detected. The initial weight of the filter could therefore be used.

Increase in the excess of reagent added, from a slight amount to 25 and 100% caused an increase in the weight of the precipitate, despite a fall in the pH of the solution (Nos. 1, 2,3). Although the actual results were higher, a similar effect due to variation of the excess of the reagent added was also observed when the mixtures were allowed to cool overnight before filtration (Nos. 4,5). Addition of ammonia after the precipitate had formed, in order to raise the pH to 5·5, caused low results, due probably to some of the zinc not being in the correct form, and the precipitates did not readily reach constant weight, even on prolonged heating. (Nos.6,7,8).

If ammonium acetate were added after the 8-hydroxyquinoline, as had been found advisable for the determination of aluminium with the reagent (86), and then a little ammonia to raise the pH slightly, difficulty in obtaining weight constancy was again encountered. In such experiments, the precipitates were found to be abnormally compact. The positive errors found (Nos.9,10) suggest contamination of the precipitates by adsorption or occlusion of the reagent, as can occur with the magnesium complex (87). A correct result was not obtained even after heating for more than 24 hours at 160°C.

In all experiments, a frothing tendency was observed when the solutions containing the precipitates were boiled, and

careful control of the heating is therefore necessary during the digestion of the precipitates.

TABLE II

Determination of Zinc with 8-Hydroxyquinoline under Various Conditions as described above.

Zinc taken in all cases = 52·75 mg

No.	Excess of reagent, %	pH of filtrate	Filtration temperature	Error 10^{-5}g
1	small	4·7	hot	-27
2	25	4·6	hot	-7
3	100	4·5	hot	+18
4	small	4·7	cold (overnight)	-11
5	25	4·65	cold (overnight)	+12
6	small	5·5	hot	-53
7	small	5·5	hot	-75
8	25	5·5	hot	-22
9	small	4·7	hot	+10
10	25	4·7	hot	+37

From these experiments it was seen that the precipitates were liable to be contaminated if the excess of reagent was large. It was therefore decided that the excess should be kept small, and an excess of 1 ml of the reagent solution was used in future experiments, this being the smallest amount readily detectable in the solutions. Since cooling of the mixture before filtration had caused a slight gain in weight of the precipitate, it was decided to cool for 30 minutes in running water before filtration. With these changes, the following final procedure was devised.

Procedure for the Determination of 5 to 50 mg of Zinc by Precipitation with 8-Hydroxyquinoline in Buffered Acetic Acid Solution —— To 60 ml of an approximately 0·2 N-hydrochloric acid solution containing 5 to 50 mg of zinc, add 5 N-ammonium hydroxide until neutral to methyl red, followed by 0·1 ml of glacial acetic acid and 6 ml of 30% w/v ammonium acetate solution. Heat to 60°C and add a 2% w/v solution of 8-hydroxyquinoline in 0·8 N-acetic acid, at the rate of 1 drop per second, until an excess of 1 ml has been added. Heat gradually to boiling and maintain at the boiling point for a few minutes. Allow the mixture to cool in running water for 30 minutes, then filter on a weighed, sintered glass filter of porosity 4. For 10 mg of zinc and upwards, use a filter crucible, and for smaller amounts of zinc, a filter-tube provided with another as a tare, which is given the same heating and cooling treatment as the filter. Transfer and wash the precipitate with about 50 ml of hot water, stirring the precipitate on the filter with a glass rod to ensure thorough washing. Dry at 160°C to constant weight.

The resulting anhydrous zinc 8-hydroxyquinolinate contains 18·49% of zinc.

Some results for the determination of various amounts of zinc by this procedure are given in Table III.

TABLE III

Zinc taken	Error	pH of filtrate	Zinc taken	Error	pH of filtrate	Zinc taken	Error	pH of filtrate
mg	mg		mg	mg		mg	mg	
52·75	-0·29	4·7	20·90	-0·10	5·1	5·68	+0·09	5·4
52·75	-0·29	4·7	21·05	+0·05	5·1	6·07	+0·01	5·4
47·18	-0·24	-	17·60	+0·02	-	5·67	+0·02	-
48·63	-0·37	-	18·29	+0·03	-	5·62	+0·04	-
Precipitation in presence of 0·8 g of ammonium nitrate								
46·39	-0·26	-	18·08	0·00	-	4·84	+0·02	-

From these results it is seen that with 5 and 20 mg of zinc there is no significant error. With 50 mg a consistent negative error of 0·3 mg occurs, and a correction of +0·30 mg has therefore been applied to all other results for the determination of 50 mg of zinc by this procedure. None of the exploratory experiments indicated a reliable means of eliminating this error, and in view of its constancy, the application of the above correction gives results adequate for the study of the anion exchange of zinc.

The Influence of Other Substances — As shown by the last three results in Table III, the addition of 0·8 g of ammonium nitrate had no effect on the results. This corresponds to the amount of nitric acid used in certain later ion-exchange experiments. (p.51 et seq.).

Only small amounts of tin^{IV} or antimony^{III}, but more lead, may be present, as shown by the following results for the determination of 5 mg of zinc in presence of these elements.

Other Metal	Tin^{IV}				Lead		$Antimony^{III}$	
Amount taken, mg.	0·3	0·5	3	5	2	2	0·5	0·75
Error on zinc, 10^{-5} g	+11	+12	+17	+19	+3	+8	+14	+5

$Antimony^{III}$ and tin^{IV} interfere by contaminating the precipitates with insoluble hydrolysis products, which may cause considerable slowness in the filtration without much affecting the weight of the precipitate. 0·5 Mg of tin^{IV} is the maximum amount which may be present before the filtration is seriously impeded.

$Antimony^{V}$ was found to be so slowly hydrolysed that 10 mg did not affect the determination of 5 to 50 mg of zinc.

Although more subject to interference than the precipitation in alkaline tartrate solution (p.39 et seq.), the method described above is simpler and therefore preferable to the other when interfering elements are absent.

PRECIPITATION IN ALKALINE TARTRATE SOLUTION

According to Berg (46) only the metals of the 'oxine group', namely zinc, cadmium, $copper^{II}$, magnesium and $iron^{II}$ are precipitated by 8-hydroxyquinoline from alkaline tartrate solutions. Zimerman and Wenger (88), studying the method for the determination of zinc in such solutions on the micro-scale, found that interference could occur in the presence of $chromium^{III}$, $cobalt^{II}$, or nickel, although these would not be expected to precipitate. Interference will also occur in the presence of those metals which precipitate as hydroxides from alkaline tartrate solutions, e.g., beryllium, indium and titanium. Nevertheless, the method is the most selective of those with 8-hydroxyquinoline. $Iron^{III}$, aluminium, tin^{IV}, antimony, bismuth, etc. which interfere in the precipitation in buffered acetic acid solution are almost without

influence. The interference due to copper may be eliminated by complexing it with cyanide (76) or with thiourea and iodide (89 - this method was published after the investigation had been concluded). However, as a correction for the small amount of copper contaminating a zinc 8-hydroxyquinolinate precipitate after an ion-exchange experiment could readily be applied (p. 52), no investigation of means for eliminating it during the precipitation was made.

The following procedure derived from those of Berg was used in a number of exploratory experiments.

To the solution (60ml, ca. 0·2 N in hydrochloric acid) containing 5 to 50 mg of zinc, add 1 g of tartaric acid, and 2 N-sodium hydroxide solution until an excess of 5 - 10 ml beyond the neutral point (phenolphthalein) is present. Precipitate the zinc in the cold by the addition, at the rate of 1 drop per second, of 15 ml of a fresh 3% w/v solution of 8-hydroxyquinoline in alcohol, heat to 60°C until the precipitate settles and becomes crystalline, then filter and wash the precipitate with hot water. Dry at 160°C to constant weight.

Certain difficulties were encountered from the first. The precipitates formed films on the wet glassware which were not readily removed by the washing water; addition of a trace of sodium tauroglycocholeate was found to prevent this (90). If the clean sintered glass filter were weighed both before and after an experiment, a significant loss in weight, in general of about 1 mg but occasionally of up to 5 mg, was detected. This loss in weight occurred during the period of contact of the filter with the hot alkaline solution, not during the treatment with acid used to remove the precipitate. The final weight of the filter was therefore required. For

the dissolution of the precipitates from the filters, a 1:2 v/v mixture of concentrated hydrochloric acid and ethanol was found to be more effective than dilute aqueous acid or chloroform, with which dissolution was slow or incomplete.

When these necessary modifications to the procedure were incorporated, the results for ca. 50 mg of zinc were erratic, and for ca. 10 mg persistently low, in one case by as much as 4·5 mg. Further careful examination of the method was therefore necessary.

As the low results might be due to the pH of the solutions (12·5) being too high, some experiments were carried out in which the pH was lowered to about 9 or 10 by the cautious addition of a tartaric acid solution after the precipitation, but the results were not much improved and the precipitates were very difficult to filter. The pH had to be at least 12 before a precipitate of satisfactory character was obtained. Berg (47) and Fleck and Ward (91) state that precipitation is quantitative up to pH 13·4, and a pH of ca. 12·5 should therefore be safe.

Variation of the amount of tartrate over the range 0·5 to 5 g of tartaric acid had no noticeable effect.

Since the amount of reagent employed for 10 mg amounts of zinc represented a very large excess, an experiment was carried out with only a slight excess added, and a small positive error was found. As the most obvious reason for the increased weight of the precipitate was the reduction in the amount of alcohol added as solvent for the 8-hydroxyquinoline, an experiment was then carried out with a similar small excess of the reagent, but with the solution after precipitation arranged to contain about 50% by volume of alcohol. Only a slight amount of precipitate was produced. A similar inhibition was found if acetone were

substituted for the alcohol.

A change was therefore made to the use of a 2% solution of 8-hydroxyquinoline in sodium hydroxide, thus eliminating the organic solvent. There was evidence of a distinct improvement in the results, and experiments were then devised to select the conditions to be used finally for the determination of zinc. The results for these experiments are shown in Table IV, (p. 38).

With small amounts of zinc, under 10 mg, it was found, as had been stated by Berg, that precipitation did not occur immediately on addition of the reagent, and for such amounts of zinc it was decided always to add an amount of 8-hydroxyquinoline which would be adequate for the precipitation of 10 mg of zinc. For larger amounts of zinc, where precipitation occurred readily in the cold, addition of an excess of the reagent could be more easily controlled, 0·5 ml excess being readily detectable. Increase of the excess from this amount to 3 ml (25%) caused a slight increase in the results for 50 mg of zinc, but with 20 mg a 10 or 50% excess made no difference (Nos. 1,2,3,4,9,10). With 50 mg of zinc, cooling of the solution after precipitation caused a slight increase in the weight of the precipitate (No. 2). In all other experiments, the solutions were filtered while still hot. The precipitates were found to settle better and to be more easily filtered if the heating were carried out at 70 - 80°C instead of 60°C. With small amounts of zinc, it did not matter whether the solutions were allowed to stand in the cold until precipitation was complete, or were heated immediately after addition of the reagent (Nos. 13, 14).

As found by Berg, the excess of alkali had to be controlled. With 5 or 20 mg of zinc, a 5-ml excess of 2 N-sodium hydroxide was adequate, but with 50 mg the excess had to be increased to

6·6 ml before all the zinc hydroxide dissolved. Increase of the excess to 8 ml caused negative errors in the determination of the smaller amounts of zinc, but had little effect on 50 mg (Nos. 5,6,11,12,15,16). Negative errors were encountered if this amount were precipitated in the presence of 15 or 25 ml excess alkali (Nos. 7,8).

TABLE IV

Determination of Zinc with 8-Hydroxyquinoline under Various Conditions as described above.

No.	Zinc taken, mg	Excess of 2N-NaOH, ml	Excess of reagent, %	Error, 10^{-5} g
1	52·75	6·6	small	+37
2	52·75	6·6	small	+54 *
3	52·75	6·6	25	+60
4	52·75	6·6	25	+65
5	48·25	8	small	+19
6	48·57	8	small	+26
7	52·75	15	small	-50
8	52·75	25	small	-186
9	20·51	5	10	+16
10	20·88	5	50	+16
11	17·54	8	10	-40
12	18·92	8	10	-33
13	5·21	5	100	+10 †
14	5·29	5	100	+11 ‡
15	5·18	8	100	-63
16	4·58	8	100	-38

* Allowed to cool before filtration
† Allowed to stand in cold until precipitation was complete before heating
‡ Heated immediately after addition of reagent.

From the results of these various experiments, the following procedure was derived as suitable for the determination of 5 to 50 mg of zinc.

Procedure for the Determination of 5 to 50 mg of Zinc by Precipitation with 8-Hydroxyquinoline in Alkaline Tartrate Solution —— Prepare the reagent solution by adding 20 ml of hot water to 2 g of 8-hydroxyquinoline and 0·75 g of sodium hydroxide, heating if necessary until all has dissolved and then diluting to 100 ml. Use when cold and prepare fresh daily.

To 60 ml of an approximately 0·2 N-hydrochloric acid solution containing 5 to 50 mg of zinc, add 1 g of tartaric acid and 0·05 ml of 0·002% w/v o-cresolphthalein solution (in alcohol). Add 2 N-sodium hydroxide (carbonate free) until the indicator becomes pink, and then 5 ml in excess. If the amount of zinc is near the maximum, increase this excess, if necessary, to 6·6 ml in order to dissolve all the zinc hydroxide. To the cold solution add 3 - 5 mg of sodium tauroglycocholeate and then add the reagent solution, prepared as above, at the rate of 1 drop per second, until an excess of 0·5 ml is present. For small amounts of zinc, under 10 mg, add 2·5 ml of the reagent solution. Digest the mixture at 70 - 80°C for 30 minutes, in order to induce the precipitation of small amounts of zinc and to flocculate any precipitate already present. Filter hot through an unweighed sintered glass filter, porosity 4, and transfer and wash the precipitate, stirring it on the filter with a glass rod, with about 50 ml of hot water. Dry at 160°C to constant weight. Dissolve the precipitate in 1:2 v/v concentrated hydrochloric acid - ethanol solution, wash, dry and weigh the filter.

The precipitate after drying contains 18·49 % of zinc.

(Note. The change to the use of o-cresolphthalein as indicator was made because a fading tendency had been observed with phenolphthalein. If too much indicator is added, the detection of the presence of excess of the reagent is difficult, but the amount specified above causes no trouble.)

Some results for the determination of various amounts of zinc are given in Table V, from which it is seen that the method is sufficiently satisfactory for use in the examination of anion-exchange separations.

TABLE V

Zinc taken, mg	Error, mg
47·67	+0·09
48·40	+0·03
18·15	+0·12
17·91	-0·09
5·35	-0·04
5·37	-0·04

The Influence of Other Metals — As the results in Table VI (p.41) show, large amounts of tin^{IV} could be tolerated, except perhaps with the smallest amounts of zinc, where contamination of the precipitates by hydrated stannic oxide made filtration very slow. As this contaminant did not dissolve in the hydrochloric acid - ethanol mixture, the weight of the zinc complex determined was not affected.

TABLE VI

Zinc taken, mg	Tin taken (approx.), mg	Error on Zinc, mg
46·97	50	+0·33
48·99	50	+0·05
18·15	80	-0·03
17·70	80	+0·07
4·71	100	+0·15
5·86	100	+0·11

No precipitate was given by 100 mg of iron^{III} in cold or hot solutions. 5 Mg of cobalt^{II} were partially precipitated in hot solutions and only a small amount could therefore be tolerated. Uranium^{VI} caused interference by precipitating as, presumably, sodium uranate.

With these two reasonably reliable procedures for the determination of 5 to 50 mg of zinc with 8-hydroxyquinoline, a quantitative investigation of the anion-exchange separation of zinc from other elements was now undertaken.

A recent book by Hollingshead (92) gives much useful information concerning the applications of 8-hydroxyquinoline in the analysis of materials for zinc.

THE SEPARATION OF ZINC FROM SOME OTHER METALS BY ANION EXCHANGE, IN RELATION TO ITS DETERMINATION WITH 8-HYDROXYQUINOLINE

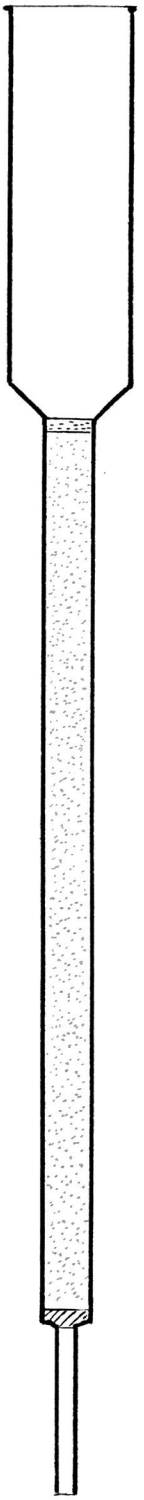
With the previously decided scale of operations (p. 26), it was desirable to be able to separate up to 50 mg of zinc from aluminium, cadmium, copper, lead, magnesium and tin in amounts up to 100 mg including the zinc; manganese and nickel up to at least 30 mg; and several other metals, e.g. cobalt, iron, calcium, beryllium, etc. up to at least 5 mg. These amounts cover the requirements with a large number of zinc-containing materials. While some of these elements could be eliminated by choice of suitable conditions for the determination of zinc with 8-hydroxyquinoline, the desire for a method of the widest possible application required their inclusion in any comprehensive study of a separation procedure. From the results of the preliminary small-scale experiments previously described (p. 24), it was apparent that if 2 N-hydrochloric acid and water were used for the adsorption and elution of zinc, respectively, a column of strong-base anion-exchange resin would serve for the separation of zinc from many other elements. Indium and cadmium would not be completely eliminated, but since indium is a rare constituent of zinc-containing materials, and many materials contain zinc but no cadmium, these elements were meantime excluded from consideration.

The original tentative method which it was hoped to use consisted in applying to a resin column in the chloride form, in equilibrium with 2 N-hydrochloric acid, a small volume of a solution containing the zinc and other metals as chlorides in that acid, then washing aith the same acid until non-adsorbed

and weakly adsorbed ions were eliminated. This treatment would leave on the resin zinc, bismuth, mercury and perhaps other elements in their entirety, together with traces of copper. On washing with water, it was hoped to obtain the zinc (plus the trace of copper) in the effluent and to leave behind the other elements initially adsorbed.

Selection of Conditions for Column Operation — The resin, Amberlite IRA-400, which had been used in the preliminary experiments was now compared with certain other anion-exchange resins, e.g. Amberlite IR-4B, Dowex-2, De-acidite E and De-acidite FF, and found to be the most suitable for anion exchange of zinc from 2 N-hydrochloric acid solutions. The resin, which is supplied in the hydroxyl form, consists mainly of spheres of 10 to 50 mesh. For analytical use smaller particle sizes are generally desirable (93), but decrease in particle size increases the resistance to flow of liquid and therefore the time required for operations with the columns. It was found that with resin ground and seived, the fraction -50+100 mesh gave a satisfactory uptake of zinc combined with a reasonably rapid flow. The air-dried resin in the (OH) form was slightly ground, and the selected material converted into the chloride form by soaking overnight in 2 N-hydrochloric acid at 40 C. 'Fines' were removed by repeatedly washing by decantation with that acid, and the resulting slurry was used for the packing of columns.

Since 5 mg of zinc had been completely adsorbed on a small column as used for the preliminary experiments, it was thought that a column of similar length (10 cm) with the cross-section increased ten-fold, would allow of the complete adsorption of



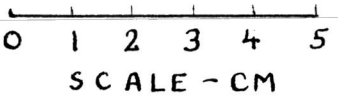


FIGURE 3

up to 50 mg of zinc. Some loss of zinc occurred, however, and columns of 15 cm length and 7 mm diameter, containing about 3 g of resin were therefore used. Pyrex glass tubes were constructed to the dimensions in Fig. 3. The resin was supported on a plug of glass wool or a sealed-in coarse sintered glass disc, and retained by a plug of cotton wool, which also prevented the columns from running dry. For the preparation of a column, the tube was filled with 2 N-hydrochloric acid and then sufficient of the resin slurry was poured in to give the required depth of bed. The cotton wool plug was then packed in position, any resin washed out of the cup at the top of the column, and the column washed by the passage of 20 ml of 2 N-hydrochloric acid. Experiments were performed at room temperature (17°C), and, with resin of the selected particle size, the flow-rate was approximately 3 ml cm^{-2} min^{-1}. Constant-head bulbs were used for washings with large volumes of liquid.

As the results of Kraus and Moore showed that the optimum acidity for the adsorption of zinc by an anion-exchange resin from hydrochloric acid solution was 2 N, it was decided to use exactly 2 N acid. At lower concentrations there was a risk of loss of zinc, and at higher concentrations, while the risk of loss of zinc was less, the adsorption of other elements, notably copper, would be expected to increase.

Preliminary Experiments on the Larger Resin Columns — On applying 5 ml of a 2 N-hydrochloric acid solution containing 50 mg of zinc to a column, the resin being in equilibrium with that acid, and washing further with the same acid, the first 50 ml of the effluent was found, after evaporation to dryness

and testing with copper sulphate and ammonium mercury(II) thiocyanate, to contain less than 0·01 mg of zinc. Probably 75 ml of acid could be used without significant loss of zinc.

Similar tests were carried out in order to find out how much water would be required to elute the adsorbed zinc, and 20 ml were found to elute over 80%. After 60 ml of water had been used, two further 20-ml portions were found to contain 0·02 and less than 0·01 mg of zinc, respectively. 60 ml of water were therefore considered adequate.

It was thought that 50 ml of the acid would effectively remove up to 100 mg of cobalt^{II}, nickel, manganese^{II}, titanium^{IV}, uranium^{VI}, or beryllium, and almost all copper^{II}. Iron^{III} was found to be almost completely eluted, but a little remained on the resin. Further experiments showed that aluminium, magnesium, thorium, zirconium, chromium^{III} and calcium were not appreciably adsorbed. All of 100 mg of tin^{IV} or of 50 mg of antimony^{III} or bismuth were thought to remain on the columns, but with antimony^{V}, about 25% was eluted. Lead chloride in the amount required to saturate 5 ml of 2 N-hydrochloric acid was held by the resin.

On subsequent elution with 60 ml of water, of the elements other than zinc adsorbed from 2 N-hydrochloric acid solutions, 100 mg of tin^{IV} were found to yield 20 mg; 50 mg of antimony^{III}, 2 mg; 50 mg of antimony^{V}, 10 mg; a few mg of lead, 1 mg; and 50 mg of bismuth, nil to the eluate. Traces of copper and iron were eluted. None of these elements in the amounts quoted would be expected to interfere seriously with the determination of zinc with 8-hydroxyquinoline in alkaline tartrate solution. The trace of copper would be precipitated, but could be readily tested for in the precipitate. It therefore seemed possible

to evolve a generally applicable method for the determination of zinc originally in association with many other elements.

QUANTITATIVE EXPERIMENTS WITH ZINC ALONE AND IN ASSOCIATION WITH OTHER ELEMENTS

The following procedure was adopted in order to test quantitatively the adsorption of zinc by and its recovery from the resin columns.

To a column of resin (15 cm x 7 mm ϕ), in equilibrium with 2 N-hydrochloric acid, apply 5 ml of a 2 N-hydrochloric acid solution containing 5 to 50 mg of zinc in a total of not more than 100 mg of metals. Wash the container with five 1-ml portions of the acid, which are transferred to the resin column, and continue washing the resin until a total of 50 ml of the acid has passed through. Reject the effluent. Elute the zinc by the passage of 60 ml of water and determine it by the appropriate method with 8-hydroxyquinoline previously described (pp.32, 39). If no other adsorbable metals were present, regenerate the column by passing 50 ml of 2 N-hydrochloric acid through it.

With this procedure, the results of the first experiments on the determination of zinc alone were sufficiently satisfactory to justify a preliminary examination of the behaviour of zinc initially in the presence of other metals. In experiments involving the separation of the smaller amounts of zinc from metals which were not significantly held by the resin, a few rather large negative errors occurred. In general, columns had been regenerated as described above when this was considered safe, but fresh columns had been brought into use at intervals. The more significant errors were found to be associated with the latter, and a more thorough investigation was therefore

made of the behaviour of zinc alone, on fresh resin and on regenerated resin, in an attempt to discover the source of the irregularities. With fresh resin columns, the amounts of zinc lost, from 50 and 5 mg initially applied, ranged from 0·1 to 0·7 mg, and from 0·04 to 0·4 mg, respectively. Comparable losses were encountered with a different batch of resin. Decrease of the flow-rate through the columns to 1·5 ml cm^{-2} min^{-1} did not effect any improvement.

The lost zinc was not found in the acid effluent, and in an experiment in which 50 mg of zinc had been used and 0·34 mg had gone amissing, only 10% of this amount was recovered on washing with a further 40 ml of water. Elution with 0·005 N-hydrochloric acid was tried, in case slight hydrolysis was responsible for the loss of zinc, but no improvement was indicated. Some results for the determination of zinc alone, from fresh and regenerated resin columns are given in Table VII.

TABLE VII

Zinc taken (approx.),	Fresh Resin. Error,	Regenerated Resin. Error,
mg	10^{-5} g	10^{-5} g
50	-12, -31, -72, -34, -15, -34	+2, -24 -30, -11
20	-12, -17	-5, -8
5	-41, -15, -18, -23, -4, -33*, -20*	-6, +7

* Flow-rate reduced to 1·5 ml cm^{-2} min^{-1}.

The Use of Resin pre-saturated with Zinc —— Since zinc was evidently sometimes retained on the resin, experiments were performed to find out what effect was produced by the use of resin that had previously been treated with an excess of zinc chloride. Resin in the chloride form was soaked overnight in an excess of a solution of zinc chloride in 2 N-hydrochloric acid and a column was prepared from the suspension. The resin was washed with 2 N-hydrochloric acid and then with 60 ml of water. In further 20-ml water washings, a significant amount of zinc (0·05 mg) was found only in the first. The resin was left in contact with water overnight and then 50 ml of 2 N-hydrochloric acid were passed through and tested for zinc, 0·05 mg being found. Further treatments with 60 ml of water and 50 ml of acid yielded 0·1 and less than 0·01 mg of zinc, respectively. A final water-washing, after the resin had been in contact with the acid for three days, gave 0·05 mg of zinc. These results showed how tenaciously a small amount of zinc was held by the resin.

Two columns of zinc-saturated resin were repeatedly treated alternately with water and 2 N-hydrochloric acid before they were used to test the recovery of 5-mg amounts of zinc that were applied to them in the usual way. Negative errors, similar to the maximum previously recorded for this amount of zinc, were found. This showed that the resin, initially saturated with zinc, had, for all practical purposes been freed from zinc by the successive water and acid treatments, and was reclaiming some from the test solution.

Water was left in both columns overnight and then 50 ml of 0·005 N-hydrochloric acid were passed through, with removal of

about 0·05 mg of zinc. Further washing of one column with 20 ml of 0·25 N-sulphuric acid yielded 0·05 mg of zinc, and of the other with two 20-ml portions of 0·25 N-nitric acid, 0·1 and 0·05 mg of zinc respectively. It was therefore confirmed that some zinc may become attached to the resin in a manner different from the rest. Since the amount retained will presumably be related to the period of contact of the resin with water, it seemed that correct results might be obtained with the test solutions if the zinc-treated resin were so handled beforehand that none of the firmly held zinc was detached. Accordingly, columns prepared from zinc-saturated resin were, after washing with 20 ml of 2 N-hydrochloric acid and 100 ml of water, immediately treated with 50 ml of 2 N-hydrochloric acid. These columns were used for experiments with 50 and 5-mg amounts of zinc. The recovery of zinc was quantitative, the errors for 50-mg amounts being +0·01 and +0·08 mg, and for 5-mg amounts, nil and +0·01 mg. Since resin columns prepared in this way had yielded an amount of zinc similar to that detached from columns through which 5 mg of zinc had been passed, and also to the average amount that had gone amissing in the passage of 50 mg of zinc, it was evident that columns to which 5 to 50 mg of zinc had been applied, and from which the bulk of the zinc had afterwards been removed with water, should, if regenerated immediately with 2 N-hydrochloric acid, give similar results. This was confirmed.

TABLE VIII

DETERMINATION OF ZINC IN MIXTURES AFTER SEPARATION BY ANION EXCHANGE

(Elution with Water only)

Zinc taken (approx.),	Other Metals		Fresh Resin, Error,	Regenerated Resin, Error,	Zinc pre-saturated Resin, Error,
mg		mg	10^{-5} g	10^{-5} g	10^{-5} g
50		50	-	+4, -16	+6, +10
20	Al	80	-	+1, -14	+10, -19
5		100	-	-2, -12	+23, -11
50		50	-4, -16	-13, -14	-
20	Mg	80	-1	+1	-
5		100	-5, -4	-	-
50		50	-	+19, -25	-
20	Cu	80	-	-3, -7	-
5		100	-38, -38	-1, -2	-
50	Co^{II}, Ni	50	-9, -7	-	+28, -35
20	and Mn^{II}	80	-19, -12	-	+7, -5
5	(1:2:2)	100	-8, -15	-	-8, +9
50	Fe^{III}, Be, Ca,	20	-	-5, +12	-
20	and Ti^{IV}	20	-	-11, +20	-
5	(1:1:1:1)	20	-	+6, +10	-
50		50	-	-8*, +9*	-
20	Sn^{IV}	80	-	-23*, -13*	-
5		100	-	-34*, -5*	-
50		50	-	-63	-
20	Bi	50	-	-26	-
5		50	-	-12	-
50		50	-	+39*	-
20	Sb^{III}	50	-	+15*	-
5		50	-	-9*	-
50		50	-11	-	-
20	Sb^{V}	50	-22	-	-
5		50	-31	-	-
50	Sb^{III}, Bi, Th,	25	-	-27	-
20	Zr and Cr^{III}	25	-	-24	-
5	(1:1:1:1:1)	25	-	-17	-

* Precipitated with 8-hydroxyquinoline in alkaline tartrate solution.

The Determination of Zinc in Mixtures —— In Table VIII are recorded for convenience all the results hitherto obtained for the determination of zinc in mixtures. Most experiments relate to fresh resin columns, or to resin regenerated without particular attention having been paid to the period during which the resin had stood in contact with water beforehand. In the last column are some results for experiments made with resin that was immediately regenerated after the passage of at least 5 mg of zinc. With reference to the results for mixtures that left negligible amounts of other metals on the resin, it is evident that the use of zinc pre-saturated resin has effected little improvement and that there is a lack of precision throughout. No evidence has been obtained that repeated use of a column gives better results, and the irregularities which appear cannot be explained.

THE ELUTION OF ZINC BY MEANS OF DILUTE NITRIC ACID

As the attempt to counteract the error due to the retention of a variable residue of zinc by the resin had only partially succeeded, a means of ensuring complete removal of zinc was next sought. Since 0·25 N-nitric acid eliminated the firmly attached zinc much more readily than water, and more effectively than 0·25 N-sulphuric acid (p. 49), its use for breaking down and removing the zinc complex from the resin was examined. Elution with water had caused retention of bismuth and much tin and antimony by hydrolysing their salts, therefore 20 ml of water were first applied and then sufficient 0·25 N-nitric acid to eliminate the rest of the zinc. 40 Ml was found to be a safe excess.

In Table IX are given the results for several experiments on the determination of zinc alone. 20 ml of water and 40 ml of 0·25 N-nitric acid were used for eluting it from the resin and precipitation with 8-hydroxyquinoline was effected in buffered acetic acid solution.

TABLE IX

Approximate Weight of Zinc taken, mg	Error 10^{-5}g
50	+18, -17, +30, -11, +6
20	+4, +9
5	+6, +3, +6, +3

While the results are seen to be of reasonable precision, the tendency for positive errors to occur suggests that traces of metallic impurities, most likely copper and iron, are intruding. Iron could be eliminated by precipitation of the zinc in alkaline tartrate solution, but copper would not be eliminated without further complexing (76,89).

On examination of the effect of the above change in procedure on the other metals adsorbed by the resin from 2 N-hydrochloric acid solutions, no important change was found with tin^{IV}, lead or antimony^{V}. The amount of antimony^{III} accompanying zinc was doubled and 2 to 3 mg of bismuth were obtained from 5 to 50 mg initially applied. Contamination by iron and copper was greater. By direct quantitative test, 100 to 5 mg of copper, in the presence of some zinc, were found to yield 0·2 % of the amount initially applied to the eluate containing zinc.

Similarly, 100, 10, 5 and 0·5 mg of iron^{III}, the last three in association with 10 mg of zinc, gave 0·6, 0·07, 0·04 and 0·015 mg, respectively. A blank run with 10 mg of zinc and no added iron gave 0·002 mg of iron. On occasion, however, larger amounts of iron were noted than would be predicted from these results, indicative of some erratic effect.

Apart from copper, none of these elements in the amounts quoted would yet be expected to interfere in the determination of zinc with 8-hydroxyquinoline in an alkaline tartrate solution. In the case of copper, the fraction of the initially applied copper appearing in the water-nitric acid eluate was essentially constant, and if the amount of copper originally present were known, a suitable correction could easily be applied.

It seemed, therefore, that with the use of water and nitric acid for elution of the zinc, reasonably accurate results for the determination of zinc in mixtures would be obtained. The following procedure was therefore finally adopted.

Procedure for the Separation of Zinc by Anion Exchange prior to its Determination with 8-Hydroxyquinoline - Procedure 'A'. Prepare a resin column (see p. 44), wash with 20 ml of 2 N-hydrochloric acid, 50 ml of 0·25 N-nitric acid and 50 ml of 2·0 N-hydrochloric acid in that order. Transfer to the column about 5 ml of a 2 N-hydrochloric acid solution containing up to 50 mg of zinc and a total of not more than about 100 mg of metals, and allow the solution to percolate into the column. Rinse the container five times with 1-ml portions of 2·0 N-hydrochloric acid, allowing the column to drain between additions, and then add more of the acid to bring the total volume of solution added to 50 ml. Reject the effluent. Now elute the zinc by allowing

TABLE X

DETERMINATION OF ZINC IN MIXTURES AFTER SEPARATION BY ANION EXCHANGE

(Elution with Water and 0·25 N-Nitric Acid)

Zinc taken (approx.),	Other Metals		Error,
mg		mg	10^{-5} g
20	Al	80	+3, +1
5		100	-1, +3
50	Mg	50	-12, -11*
20		80	-3*
5		100	+4, (-43*), +4*, +3*
50	Cu	50	-18‡
5		100	+13‡
50	Co^{II}, Ni, and Mn^{II} (1:2:2)	50	-21, +3
20		80	+2, +6
5		100	+11, +8
50	Fe^{III}, Be, Ca, and Ti^{IV} (1:1:1:1)	20	0*
20		20	+8‡, +3*
5		20	+5‡, +7*
50	Cr^{III}, Th, U^{VI}, and Zr (1:1:1:1)	20	+4
20		20	+5
5		20	+13
50	Sn^{IV}	50	-54*
20		80	-30*
5		100	-26*
50	Bi	50	-4*
5		50	-12*
50	Sb^{III}	50	-8*
5		50	-2*
50	Sb^{V}	50	-12
5		50	+4

* Precipitated with 8-hydroxyquinoline in alkaline tartrate solution.

‡ Corrected for predicted copper contamination (p. 52).

‡ Corrected for iron, 0·05 and 0·18 mg, respectively, found on examination of the precipitates.

20 ml of water, followed by 40 ml of 0·25 N-nitric acid to percolate through the column. Collect the solution and proceed with the determination of zinc by the appropriate method (pp. 32, 39). Precipitation of zinc 8-hydroxyquinolinate in alkaline tartrate solution is generally applicable. Precipitation in buffered acetic acid solution is simpler and, with reference to the information given on pp.33 and 52, may be used for materials that contain no bismuth, a limited amount of iron and less than 2 % of tin or antimony. Whichever method is used, a correction is required for copper, and when precipitation in acid solution is adopted, it is desirable to examine the precipitated for the presence of iron. For 50-mg amounts of zinc, precipitated in acid solution, a correction of +0·30 mg is required (p. 33).

Reject the resin if the original solution contained metals (e.g., lead, antimony, bismuth, tin) that are retained by it. Otherwise prepare the column for further use by immediately passing through it 50 ml of 2·0 N-hydrochloric acid.

The results for numerous separation experiments carried out by the above procedure are presented in Table X. Comparison of these results with those obtained previously, when water only was used for elution of the zinc (Table VIII, p. 50), shows that the errors are now less regularly negative. Where sufficient experiments have been done, the precision is seen to be improved. The actual mean errors for the results for 50, 20 and 5 mg of zinc are -0·12, -0·01 and +0·02 mg, and the corresponding standard deviations are 0·20, 0·12 and 0·10 mg respectively. The particularly good separations of zinc from aluminium and magnesium are to be noted. If either of these elements had accompanied the zinc, aluminium 8-hydroxyquinolinate would have

precipitated in buffered acetic acid solution and the magnesium complex in alkaline tartrate solution, causing positive errors, whereas the actual errors found are small or negative. As previously stated (p. 53), the behaviour of iron is erratic and precipitation in alkaline tartrate solution is recommended if iron is present. Traces of iron were frequently detected, causing discoloration of the precipitates obtained in buffered acetic acid solutions, and may well be responsible, in part at least, for the small positive errors found in some experiments where no iron was deliberately introduced.

It is noticeable that the use of nitric acid improves the recovery of zinc from mixtures containing bismuth, but the reverse effect occurs with tin, which suggests that some zinc is being trapped on the resin by the tin. This error would probably be reduced by eliminating part of the tin by volatilisation as a tin (IV) halide before the anion-exchange separation. An alternative chemical procedure is described later (p.70).

ANALYSES OF ALLOYS

In the course of the investigations, some alloys, with, in two cases, additional zinc to raise the content to the minimum under consideration were analysed. In some experiments, water only was used for elution and in others, water and nitric acid were employed. The alloys were treated as follows.

Procedure for Preparation of Alloy Solutions —— Disintegrate 100-mg amounts of alloys, containing not more than 50 % of zinc, with hydrochloric and nitric acids. Eliminate nitric acid by evaporation to dryness in the presence of an excess of hydrochloric acid and dissolve the residue as far as possible, heating if

necessary, in 5 ml of 2·0 N-hydrochloric acid. If lead is present, cool to *ca.* 0 °C to remove as much lead chloride as possible; otherwise, cool to room temperature. Apply the solution to the resin column, decanting carefully from any insoluble matter, and wash the container, and the residue, if any, with five 1-ml portions of 2·0 N-hydrochloric acid, applying the washings to the column. Any lead chloride or other solid which has passed over and been retained by the cotton wool plug should now be removed by washing out the column cup with a jet of 2 N-hydrochloric acid, after which further washing of the column with that acid and elution of the zinc are performed as on p. 53.

At a later stage it became desirable to find whether the separation of less than 5 mg of zinc would be practicable, and a bronze and an aluminium alloy yielding half this amount were included, the final determination of zinc being effected in the customary manner, but on an appropriately reduced scale. The water-nitric acid eluates in these experiments were evaporated to dryness (5 ml of concentrated hydrochloric acid being added in the case of the bronze to volatilise some tin (IV) and prevent formation of metastannic acid), and the residues taken up in 2·5 ml of 2 N-hydrochloric acid and diluted to *ca.* 30 ml with water. Precipitation with 8-hydroxyquinoline was effected as previously described (pp. 32, 39) but with only half the prescribed volumes of reagents. Weighings were performed on a semimicro-balance. Because of the high tin content, the determination of zinc in the bronze was carried out in alkaline tartrate solution. As the risk of faulty adjustment of the alkalinity was greater on the small scale, precipitation in buffered acetic acid solution was

TABLE XI

DETERMINATION OF ZINC IN ALLOYS

Alloy	Approximate composition									Zinc found	
	Cu %	Sn %	Fe %	Pb %	Al %	Mn %	Mg %	Ni %	Sb %	Zn Actual %	After elution with water %	After elution with water and nitric acid %
Manganese Brass No. 179	59	2	1	1	2	1	-	1	-	33·9*	33·5, 33·6	33·8†‡, 33·7†‡
Brass No. 37b	70	1	0·2	1	-	-	-	<1	-	27·09§	26·9, 27·2	
Bronze No. 183, with added zinc	83	10	0·1	2	-	-	-	-	<1	(1) 5·01*	4·95†	-
										(2) 5·18*	5·26†	
Bronze No. 207	87	10	0·1	<1	-	-	-	<1	≪1	2·53*	2·28†, 2·24†	2·46†‡, 2·40†‡
Aluminium alloy	1	-	0·3	-	89	1	3	-	-	5·80//	5·70, 5·78	5·97, 5·81
Aluminium alloy No. 181, with added zinc	Essentially as below									(1) 5·26*	5·24	-
										(2) 5·53*	5·60	
Aluminium alloy No. 181	5	≪1	0·5	2	87	-	1	2	-	2·37*	-	2·40‡, 2·41‡

* British Chemical Standard certificate value plus added zinc where required, (1·86 % of zinc in bronze No. 183).

† Precipitation with 8-hydroxyquinoline in alkaline tartrate solution.

‡ Corrected for copper (0·2 % of the original copper content of the alloy) - see p. 52.

§ U.S.A. Bureau of Standards certificate value.

// Value supplied by the British Aluminium Company.

‡ Corrected for copper and iron by direct quantitative test.

preferred for the aluminium alloy, which contained an insignificant amount of tin. The precipitates here were afterwards examined quantitatively for iron and copper and corrections applied, namely for 6 µg of iron and 10 µg of copper in the first precipitate and for 8 µg of each element in the second.

All results are shown in Table XI. The results obtained by elution with water are to be compared with those in Table VIII, p. 50. The results in the last column of Table XI are similarly comparable with those in Table X, p. 54. Although some of the results in the second last column are apparently good, the method relating to elution with water and nitric acid is believed to be more reliable, and is therefore recommerned. Smaller amounts of zinc than 5 mg can obviously be dealt with, but a simpler means of determining them than precipitation of zinc 8-hydroxyquinolinate in alkaline tartrate solution would be preferred.

PRELIMINARY EXPERIMENTS ON THE SEPARATION OF 0·5-MG AMOUNTS OF ZINC FROM OTHER METALS BY ANION EXCHANGE.

As the separation of 5-mg amounts of zinc from an excess of other elements was reasonably satisfactory and a few analyses of alloys had given good recovery of 2·5 mg, it was of interest to find whether smaller quantities would be adequately recovered, and how the irregularities associated with the columns would affect them. The 8-hydroxyquinoline procedure for the determination of zinc in buffered acetic acid solution was adapted to the micro-scale as follows.

Procedure for the Determination of half-mg Amounts of Zinc with 8-Hydroxyquinoline —— Prepare a 6-ml beaker provided with a sintered glass filter-stick (porosity 4) and a similar beaker containing Pyrex glass rod as a tare. Wipe, heat and cool as described by Miller and Chalmers (86) and weigh on a semimicro-balance. Remove the filter-stick and place in the beaker about 3 ml of a solution, 0·1 N in hydrochloric acid and containing ca. 500 µg of zinc. Add 0·02 ml of 0·01 % w/v methyl red and then 5 N-ammonium hydroxide until neutral: a horizontal burette may conveniently be used. Add 0·05 ml of acetic acid (1+9) and 0·35 ml of 30% w/v ammonium acetate solution. Heat to 60°C and precipitate the zinc by the dropwise addition, from a capillary, of a 0·5 %w/v solution of 8-hydroxyquinoline in 0·2 N-acetic acid, until a 25 % excess of the reagent is present. Heat to incipient boiling, cool in running water for 30 minutes and filter via the filter-stick. Wash with two 1-ml and six 0·5-ml portions of hot water and dry at 160°C to constant weight. Dissolve the precipitate in 3 ml of concentrated hydrochloric acid-ethanol mixture (1:2 v/v), wash with a further 1 ml of this liquid and then six times with 0·5 ml of hot water. Dry and reweigh the beaker and filter-stick.

After trial determinations of 0·5-mg amounts of zinc, the water-nitric acid eluates from normal blank runs on two resin columns were evaporated and added to similar amounts of zinc, which were then determined. 0·5-Mg quantities of zinc, first alone and then in association with 100 mg of aluminium or magnesium were next adsorbed on the resin and eluted with water and nitric acid in the usual way. The eluates were evaporated to small bulk, transferred by capillary to 6-ml beakers, and

TABLE XII

DETERMINATION OF APPROXIMATELY 0·5-MG AMOUNTS OF ZINC UNDER VARIOUS CONDITIONS

Remarks	Weight of zinc taken, µg	Weight of zinc found, µg	Weight found in precipitate		Corrected weight of zinc found, µg	Error, µg
			Fe µg	Cu µg		
Direct determination of zinc	491	477	-	-	-	-14
	615	618	-	-	-	+3
	541	547	-	-	-	+6
	476	477	-	-	-	+1
Direct determination of zinc after addition of the blank from the resin	458	488	12	6	463	+5
	463	503	15	8	471	+8
Zinc put through the ion-exchange procedure	478	516	lost		-	-
	472	518	21	10	474	+2
Separation from 100 mg of magnesium	465	488	15	8	456	-9
	486	492	7	3	478	-8
Separation from 100 mg of aluminium	551	570	7	7	552	+1
	495	520	12	8	493	-2

evaporated to dryness in the presence of hydrochloric acid before determining the zinc as described above. Precipitation in acid solution was effected in order to ensure the recovery of likely adventitious impurity. In all experiments, except those on the direct determination of zinc, the precipitates were disintegrated with concentrated nitric and sulphuric acids and prepared for the determination of iron and copper with potassium thiocyanate and a chloroform solution of diethylammonium diethyldithiocarbamate, respectively. Both metals were found in amounts that tallied well with the positive errors recorded throughout. When corrections for them were made, it was evident, as is shown in Table XII, that the recovery of 0·5 mg of zinc was virtually complete, even in the presence of a 200-fold excess of aluminium or magnesium. Complications might arise, however, in the examination of more complex mixtures.

THE SEPARATION OF ZINC FROM CADMIUM

The procedure described in the preceding pages for the separation of zinc from other elements by means of anion exchange does not effect a separation from cadmium. In view of the close similarity exhibited by zinc and cadmium in many reactions, a simple means of separating them would be of particular interest. Several experiments were carried out in an attempt to find an adaptation of the ion-exchange procedure by which this might be achieved. No useful results were obtained by varying the concentration of hydrochloric acid used, by employing other resins, or by operating the columns at 50°C. The application of the water - nitric acid eluates from anion-exchange columns to cation-exchange columns likewise yielded no significant separation. Since the use of thiocyanate had enabled the separation of zinc and cadmium by paper chromatography and solvent extraction to be accomplished (pp. 14, 21), the use of thiocyanate was examined here also. On application of thiocyanate to cation-exchange columns on which both zinc and cadmium were adsorbed, some slight degree of separation was observed, but the method did not seem promising. An attempt to extract zinc by means of n-butyl acetate from an anion-exchange column on which zinc and cadmium had been adsorbed from 2 N-hydrochloric acid solution, and to which thiocyanate had been applied, was unsuccessful, no significant extraction of either metal occurring.

When the use of the other halide ions was examined, it was found that fluoride (used with columns of polythene) and bromide produced no marked change in behaviour, but that iodide formed with cadmium an anionic complex which was very strongly held by the resin, whereas that formed with zinc was fairly easily broken

down by water. In early experiments both potassium iodide and hydriodic acid were used, but the latter was finally selected as the presence of potassium ion might be objectionable at a later stage. In order to make effective use of the separations obtainable with 2 N-hydrochloric acid, the normal washing with that acid was given before the application of the hydriodic acid. 5 Ml of 2 N-hydriodic acid were found to be adequate for the complexing of 100 mg of cadmium. If iodine were present, the resulting I_3^- ions were strongly adsorbed at the top of the columns, and in view of the consequent risk of displacement elution of adsorbed metals, the hydriodic acid was specially prepared and kept under carbon dioxide (p. 10).

(Since the completion of this investigation, a paper on the separation of zinc and cadmium by anion exchange with solutions containing both iodide and sulphate has been published by Baggott and Willcocks (80). Their method deals with the two elements only, whereas the use of 2 N-hydrochloric acid for adsorption of zinc, cadmium, etc., followed by treatment with hydriodic acid as described herein, enables zinc to be separated from many other elements in one series of operations.)

After the washing with hydrochloric acid, the elements liable to be present on the resin in large amount include zinc, cadmium, antimony$^{III \text{ and } V}$, tin^{IV} and bismuth. Small amounts of indium, copper^{II}, iron^{III}, lead, etc. might also be present. The effect of hydriodic acid on the adsorbed elements other than zinc and cadmium was examined. Antimony^{III} and bismuth (50 mg in each case) were found to be converted into brightly coloured complexes (orange and crimson respectively), which were not eluted by water and 0·25 N-nitric acid. Antimony^{V} was almost

completely held, with the development of a purple colour on the resin: 50 mg initially applied yielded 0·5 mg on subsequent washing with water and nitric acid. Tin^{IV} formed a black complex, but the colour disappeared on treatment with water and nitric acid. The amount of tin eluted from 100 mg initially applied was increased by the use of hydriodic acid to 30 mg. No influence on the behaviour of indium or lead was noticed, and the former was meantime again excluded from further consideration. Small amounts of copper and iron were still eluted, and the correction of 0·2 % of the copper taken remained applicable.

Zinc seemed to be somewhat more strongly held on columns treated with hydriodic acid, and when elution was effected by consecutive application of 5 ml of 2 N-hydriodic acid, 15 ml of water and 40 ml of 0·25 N-nitric acid, small negative errors were found in determining 50 mg of zinc (see Table XIII, p. 67) Increase of the amount of nitric acid to 60 ml gave complete recovery of zinc. The application of a small volume of water between the washings with hydriodic and nitric acids was deemed advisable, since hydrolysis was perhaps partly responsible for the hold-up of antimony and bismuth. The removal of the iodide from the resin was found to be difficult, and the columns were therefore rejected after use. The possibility of recovery and determination of the cadmium was not investigated.

The presence of iodide in the effluents for the determination of the zinc with 8-hydroxyquinoline was found to be objectionable. The colour produced by oxidation made pH adjustment with an internal indicator difficult and detection of the presence of excess of the reagent impossible when precipitation was performed in buffered acetic acid solution. Some experiments were

performed with a constant amount of 8-hydroxyquinoline for all quantities of zinc, and, while the results were reasonably good, the precipitates were difficult to filter and showed a discoloration suggestive of some iodination of the reagent. As alkaline conditions may be used for the iodination of 8-hydroxyquinoline (94), the use of the alkaline tartrate procedure would be unlikely to overcome the interference, because the precipitates would still be contaminated with the almost insoluble 5:7-di-iodo-8-hydroxyquinoline.

It was therefore desirable to remove the hydriodic acid, which was done by evaporation of the eluates to dryness. This was a somewhat tricky operation, as, towards the end of the evaporation, an 'explosion' occurred, with the sudden evolution of much iodine. The addition of some concentrated nitric acid before evaporation was found helpful, but did not entirely eliminate the 'explosive' tendency. Evaporation by infra-red radiation from above did not help, and a hot-plate was normally employed.

From these various findings, the following procedure was developed and used to examine quantitatively the behaviour of zinc alone and in association with other elements.

Procedure for the Anion-Exchange Separation of Zinc from Other Elements, including Cadmium, prior to its Determination with 8-Hydroxyquinoline - Procedure 'B' —— Apply the solution of metal chlorides to a prepared resin column as previously described (p. 53) and wash with 2 N-hydrochloric acid to a total of 50 ml, rejecting the effluent. Wash the column first with 5 ml of 2 N-hydriodic acid (prepared as on p. 10), and then with 15 ml of

TABLE XIII

DETERMINATION OF ZINC ALONE AND IN MIXTURES AFTER SEPARATION BY ANION EXCHANGE

(Elution with hydriodic acid - water - nitric acid)

Zinc taken (approx.),	Other Metals		Error
mg		mg	10^{-5} g
50	-	-	-53*, -33* -9, -11, 0, +2
20	-	-	-6*, -4*
5	-	-	+5*, +3*
50	Cd	50	-27*, -13
20		80	-2*, +3
5		100	+2*, -10
50	Cu	50	-13†
5		100	+14†
50	Fe^{III}	10	-11‡
5		10	-1‡
50	Sb^{III}	50	-25‡
5		50	+1‡
50	Sb^{V}	50	-14
5		50	+13
50	Bi	50	-35
5		50	+10
50	Sn^{IV}	50	-24‡
5		100	-10‡

* 40 ml only of 0·25 N-nitric acid used for elution

† Corrected for 0·2 % of the copper applied.

‡ Precipitated with 8-hydroxyquinoline in alkaline tartrate solution.

water and 60 ml of 0·25 N-nitric acid. To the resulting eluate in a 100-ml beaker add 1 ml of concentrated nitric acid and evaporate on a hot-plate. In order to prevent loss of liquid when the 'explosion' occurs, cover the beaker when the volume of liquid reaches about 20 ml and raise the temperature so that the solution is just below the boiling-point. Continue the evaporation to dryness, dissolve the residue in 5 ml of hot 2 N-hydrochloric acid, dilute to 60 ml with water and proceed to the determination of zinc by the appropriate method (pp. 32, 39).

With this procedure, experiments were performed to test the recovery of zinc from the resin columns, whether applied alone or in association with the other elements adsorbed from 2 N-hydrochloric acid solutions. The results in Table XIII (p. 67) show that the recovery of zinc applied alone is essentially complete, and that with 5- or 20-mg amounts, 40 ml of 0·25 N-nitric acid gives adequate elution. The same is found in the results for experiments on the separation of zinc and cadmium. In these experiments, the completeness of the separation was checked by examining the precipitates obtained from 5 mg of zinc initially associated with 100 mg of cadmium. In tests with Cadion 2B (4-nitronaphthalene-1:1'-azoaminobenzene-4'-azobenzene), which would readily reveal the presence of 5 μg of cadmium under the conditions employed, no evidence whatsoever of cadmium was found. The hold-up of 100 mg of cadmium is therefore complete. Experiments with zinc and other metals likewise show, in most cases, essentially complete recovery. With 50 mg of zinc in association with antimony^{III}, bismuth, or tin^{IV}, somewhat larger

negative errors are encountered, which may be due to occlusion of a little zinc by a hydrolytic product of the other element concerned. In the case of tin, some contamination of the zinc 8-hydroxyquinolinate precipitates with stannic oxide was found, although 5 ml of concentrated hydrochloric acid had been added as well as 1 ml of concentrated nitric acid before the evaporation in order to volatilise some of the tin as tin(IV) chloride.

THE PARTIAL PREVENTION OF THE ADSORPTION OF TIN BY THE RESIN

Because of the need for evaporation with nitric acid if hydriodic acid were used, with consequent risk of trouble due to the formation of 'metastannic acid', some means of preventing the final association of tin with zinc was desirable. While volatilisation of a tin(IV) halide before application of the hydrochloric acid solution to the resin might sometimes be suitable, circumstances could arise where this was not desirable, or where the presence of other elements would prevent the removal of the tin. A method was therefore sought for reducing the adsorption of tin by the resin or preventing its elution afterwards.

In the presence of hydrofluoric acid in addition to hydrochloric acid (plastic columns), some indication of a reduction of the adsorption of tin (and also of indium) was observed, but the solution in which zinc would have to be determined would contain hydrochloric, hydrofluoric, nitric, and possibly hydriodic acids, and could not be easily handled. The possibility of adding to the 2 N-hydrochloric acid solutions some organic reagent likely to have a binding effect on the tin was investigated. Oxalic acid and mandelic acid caused a reduction in the amount of tin eluted, from 100 mg initially applied, by later treatment with hydriodic acid, water and nitric acid, to 20 and 15 mg, respectively. A more significant decrease, to 5 mg, was found with n-propylarsonic acid, but the complex formed with 100 mg of tin was partially precipitated from 5 ml of 2 N-hydrochloric acid. Methylarsonic acid, used in the form of the disodium salt, was found to cause a similar effect unaccompanied by precipitation. While this reduction in the amount of tin

eluted was significant, it was still not as much as might be desired. Since the arsonic acids reduced the amount of tin actually adsorbed by the resin and did not merely retard the subsequent elution, pretreatment of the resin columns with methylarsonic acid was therefore tried. With resin treated with 5 ml of a 5 % w/v solution of disodium methylarsonate, 2 N in free hydrochloric acid, before the application of 100 mg of tin with 400 mg of the reagent, and subsequent washing with hydrochloric acid and elution with hydriodic acid, water and nitric acid, only 3 mg of tin were found in the eluate. In a similar experiment where, after application of the tin solution, the column was washed with 10 ml of the 5 % methylarsonate solution and then with 2 N-hydrochloric acid, etc., as before, no significant change was observed.

For amounts of tin under 10 mg, from which, in the absence of methylarsonate, no more than 3 mg would be expected to accompany the zinc, treatment with the reagent is probably unnecessary. Titanium^{IV} and zirconium give precipitates with methylarsonic acid in 2 N-hydrochloric acid solution which would have to be removed (cf. lead chloride, p. 57). The effect of their presence on the recovery of zinc was not examined. No influence of methylarsonic acid on the adsorption of other metals has been observed.

Procedure for the Anion-Exchange Separation of Zinc from Other Elements in Presence of Moderate to Large Quantities of Tin - Procedure 'C' —— Prepare a resin column (p. 53) and treat it with 5 ml of a 5 % w/v solution of disodium methylarsonate (see p. 11), 2 N in free hydrochloric acid (5 g of $CH_3AsO_3Na_2$,

42 ml of 6 N-hydrochloric acid and water to 100 ml). To the solution of metal ions (~5 ml, 2 N in hydrochloric acid) to be applied, add 0·4 g of disodium methylarsonate and 1 ml of 6 N-hydrochloric acid, warm if necessary to dissolve, cool and apply to the resin column. Wash with 2 N-hydrochloric acid and elute zinc by means of hydriodic acid, water and nitric acid in the usual way (cf. p. 66).

This procedure, with subsequent precipitation of zinc 8-hydroxyquinolinate in buffered acetic acid solution, was applied in a few experiments with zinc - tin mixtures. The results were of moderate accuracy:

Zinc taken (approx.),	Tin taken (approx.),	Error on Zinc
mg	mg	10^{-5} g
50	50	-27, -24
5	100	+8, -5

In the experiments with 50 mg of each element, virtually no darkening of the resin was observed on addition of the hydriodic acid, suggesting that very little tin had been adsorbed. Some contamination with stannic oxide was found in the precipitates from 5 mg of zinc, but as the contaminant did not dissolve in the hydrochloric acid - ethanol mixture, the necessary correction was easily obtained. [No concentrated hydrochloric acid had been added before evaporating the eluates (cf. p. 69)].

While the use of methylarsonic acid has significantly reduced the adsorption of tin by the resin and the amount in the eluate, it has not eliminated the negative error in the determination of 50 mg of zinc (cf. Table XIII, p. 67), or the troublesome influencs on the smaller precipitates of 'metastannic acid' formed in the evaporation to remove the iodide.

SUMMARY OF ANION-EXCHANGE PROCEDURES AND THEIR APPLICATIONS

In the foregoing sections, three methods have been described for the separation of zinc from other elements by anion exchange and two for its determination with 8-hydroxyquinoline. For the determination of zinc, the alkaline tartrate procedure (p.39) should normally be applied to solutions of 'unknown' composition. For the anion-exchange separation, the water-nitric acid elution procedure ('A', p. 53) is applicable in the absence of cadmium. In presence of cadmium, the procedure with hydriodic acid in addition is required ('B', p. 66), but it takes longer because iodide must be removed before 8-hydroxyquinoline can be used. Difficulty may be encountered in presence of tin, and the use of the third procedure, with the methylarsonic acid treatment followed by hydriodic acid - water - nitric acid elution ('C', p. 71) helps to prevent trouble here. This procedure cannot be used without modification in the presence of titanium or zirconium, and unless tin is present in quantity, procedure 'B' should normally be used.

By these procedures, reasonably accurate results for the determination of 5 to 50 mg of zinc in association with various other elements have been obtained. Similar amounts of zinc in a number of materials have been determined without difficulty. For materials, the sample weight is governed by the limits of 100 mg of total metals and a 50 mg maximum of zinc. Tentative experiments with smaller amounts (500 µg) of zinc have shown adsorption and elution to be quantitative.

As many materials contain less than 5 % of zinc, it was next decided to investigate more thoroughly the separation and determination of amounts of zinc less than 5 mg, with a view to

developing a satisfactory general method. Previous experiments with less than 5 mg of zinc had involved evaporation and semi-micro- or micro-scale gravimetric determinations with 8-hydroxyquinoline. A simpler procedure was required, and ethylenediaminetetra-acetic acid was selected as a reagent which, it was hoped, would be suitable for the direct volumetric determination of zinc in the eluates from anion-exchange columns. An account of investigations of its use for determining zinc, and of the separation of small amounts of zinc from other elements prior to such determination, follows.

THE DETERMINATION OF SMALL AMOUNTS OF ZINC WITH ETHYLENEDIAMINETETRA-ACETIC ACID

Since the discussion by Schwarzenbach and co-workers (48,49) of the properties of ethylenediaminetetra-acetic acid (E.D.T.A.) and its salts as complexing agents for many metals, much use has been made of them for the volumetric determination of zinc, with which a strong complex is formed in solutions of pH 5 upwards (95). Amongst the various procedures that have been described, use is most frequently made of titration in a solution buffered at a pH of about 10, with solochrome black as indicator (96). This procedure has been adapted to the micro-scale (50,97), and several modifications for preventing the interference of other elements have been described (51,98). Of these, probably the most useful is titration in solutions which have been treated with cyanide, and the zinc-cyanide complex subsequently broken down by the addition of an aldehyde. By this means interference due to copper, cobalt, nickel, mercury, etc., which form strong cyanide complexes, may be prevented, and it is possible to titrate some other elements which are not complexed, e.g. magnesium and lead, while the zinc is bound by the cyanide, i.e., before the addition of the aldehyde, and so to render them non-interfering. Other suggested procedures include titration at pH 6·8, when magnesium does not seriously interfere (99), titration at a pH of ca. 5, with 3:3'-dimethylnaphthidine as indicator in conjunction with the ferricyanide-ferrocyanide system (100), alkalimetric titration (48), amperometric titration (101,102), and spectrophotometric titration (103).

In the present investigation it was desirable to adopt or devise a procedure that would be applicable in conjunction with

TABLE XIV

THE BEHAVIOUR OF VARIOUS ELEMENTS IN THE ION-EXCHANGE PROCEDURES

Element	Amount applied mg	Behaviour in 2N-HCl *	Amount found eluted	Procedure †	Element	Amount applied mg	Behaviour in 2N-HCl *	Amount found eluted	Procedure †
Al	100	E	nil	A	Mn^{II}	100	E	20 µg	A
Sb^{III}	50	H	4 mg	A	Hg^{II}	50	H	nil	B
			nil	B					
					Mo^{VI}	50	(E)	8 mg	B
Sb^{V}	50	(H)	10 mg	A					
			0·5 mg	B	Ni	100	E	nil	A
Be	100	E	nil	A	Pt^{IV}	50	H	2 mg	B
Bi	50	H	3 mg	A	Se^{IV}	50	E	nil	B
	100		nil	B					
					Te^{IV}	50	(E)	5 mg	B
Cd	100	H	nil	B‡					
					Tl^{III}	50	H	50 µg§	B
Ca	100	E	nil	A					
					Th	100	E	10 µg	A
Cr^{III}	100	E	nil	A					
					Sn^{IV}	100	H	20 mg	A
Co^{II}	100	E	nil	A				30 mg	B
								3 mg	C
Cu^{II}	up to 100	E	0·2 %Cu taken	A,B	Ti^{IV}	100	E	2 mg	A//
Ga	50	E	100 µg	A	W^{VI} ¶	50	E	2 mg	B
Ge	50	E	'some'	B	U^{VI}	100	E	100 µg	A
Au^{III}	50	H	nil	B	V^{IV}	50	E	nil	B
In	100	(E)	3 mg	A,B	V^{V}	50	E	nil	B
Fe^{III}	100	(E)	0·6 mg	A,B	Zn	up to 50	H	ALL	A,B, C
Pb	2-3	H	1 mg	A,B					
					Zr	100	E	100 µg	A//
Mg	100	E	nil	A					

Notes on p. 77

the use of anion exchange for the separation of zinc from other elements. It would be advantageous if the method could be applied directly to the effluents from the resin columns, and in the presence of the small amounts of other elements which are not eliminated by the prescribed anion-exchange techniques. For convenience the behaviour in the anion-exchange procedures of 50 or 100 mg amounts of many elements, some of which have not hitherto been mentioned, is summarised in Table XIV.

Tin, iron, copper and lead would be the common elements most frequantly requiring consideration in the titration, and attention was therefore given initially to the determination of 5- to 0·5-mg quantities of zinc in their presence. The disodium salt of ethylenodiaminetetra-acetic acid was used throughout this work. While this substance can be used as a primary standard (104) and the material available (B.D.H.) had a purity of 99·0 %, the procedures evolved include the standardisation of the reagent solutions with respect to zinc.

Notes to Table XIV.

* E = eluted; E = rapidly eluted; (E) = slowly eluted with tail; H = held; (H) = most held.

† Procedures as on pages specified: — A: p. 53; B: p. 66; C: p. 71.

‡ Procedure 'A' not applicable

§ Eluted as thallium (I)

// Procedure 'C' not usable without modification

¶ Applied as phosphotungstate.

VISUAL TITRATION EXPERIMENTS - I.

Preliminary experiments showed that in an ammonia-ammonium chloride buffered solution at a pH of about 10, small amounts of zinc (ca. 1 mg) could readily be titrated with a solution of disodium ethylenediaminetetra-acetate, with solochrome black as indicator. The colour change from pink to blue at the end-point was sharp and easily distinguishable. Interference was encountered if the titration were attempted in the presence of copper^{II}, iron^{III}, tin^{IV}, or lead. The first two 'blocked' the indicator, which remained in a pink form no matter how much of the titrant was added. With tin, the reaction at the end-point was very much retarded. Lead was titrated along with the zinc. The effects of copper and lead could be overcome by the use of cyanide and an aldehyde (cf. p. 75), but no obvious means of dealing with iron^{III} or tin^{IV} was available. Attempts to eliminate iron^{III} by titration with ethylenediaminetetra-acetate at a pH of about 4, with salicylic acid or thiocyanate as indicator, were unsuccessful, as the solochrome black indicator was still 'blocked' on raising the pH in order to titrate the zinc. Other complexing agents, including bis-hydroxyethylglycine, which is 'specific' for trivalent cations (105), were also tried without success. Iron (III) could be rendered non-interfering by reduction to iron (II) and subsequent formation of ferrocyanide, but it was considered that the reduction in the presence of much nitric acid introduced from ion-exchange experiments was unlikely to be complete. No interference with the titration was observed from iodide or nitrate in the amounts likely to be encountered after anion exchange.

In a hydrochloric acid solution, buffered at pH 5 by means

of sodium acetate, with the ferricyanide-ferrocyanide - dimethyl-naphthidine indicator system (100), zinc could be titrated to a good end-point, although the change from pink to colourless was less readily distinguishable than the colour change with solochrome black. Interference was again encountered from copper^{II}, iron^{III}, and tin^{IV}, but the effects of iron^{III} and tin^{IV} could be eliminated by addition of phosphate and fluoride, respectively. Fluoride alone did not adequately suppress iron. Neither reagent eliminated the interference due to copper^{II}. Several organic reagents were tried in the hope of either masking the copper or permitting its extraction with an organic solvent, but none was effective. In some cases, as with sodium diethyldithiocarbamate, matters were worsened by the presence of the organic reagent. Some interference was encountered in the presence of iodide and nitrate, so that this procedure would probably not be applicable directly to the effluents from ion-exchange columns.

Some experiments on the amperometric titration of zinc with ethylenediaminetetra-acetate in similar solutions of pH 5 were carried out, but interference from copper^{II} was again encountered.

Of the methods examined, it was felt that, provided the interference from iron^{III} and tin^{IV} could be eliminated, titration at pH 10 was most promising. Attempts to separate the zinc from iron^{III} and tin^{IV} in acid solutions such as might be obtained after anion-exchange separations, by direct extraction of its thiocyanate in presence of masking agents for the other elements were unsuccessful. Spacu and Ripan (61) had used extraction of zinc pyridine thiocyanate for separating zinc from other metals. Since copper and iron (II), but not tin or iron (III),

form extractable complexes, it was hoped that zinc could by this means be obtained in a solution where the interference of the other elements present could be eliminated by subsequent treatment with cyanide and an aldehyde. As will be described later (p.125 et seq.), this procedure enabled the separation of zinc from a number of elements, including iron^{III} and tin^{IV} to be achieved.

It seemed, therefore, that by means of anion exchange, solvent extraction of zinc pyridine thiocyanate and suitable further treatment, zinc might be obtained in a solution in which it could be accurately titrated with ethylenediaminetetra-acetate at a pH of about 10. Examination of the titration, especially in relation to such operations, was therefore necessary.

If iron^{III} were absent and tin not present in interfering amount, extraction of zinc would be unnecessary and it would then require to be determined in 60 ml of a solution containing ca. 5 ml of 2 N-hydrochloric acid and 40 ml of 0·25 N-nitric acid, or 80 ml of a solution containing somewhat more nitric acid and also ca. 4 ml of 2 N-hydriodic acid, when this acid had been applied to the resin. If chloroform extraction of zinc pyridine thiocyanate were employed, zinc might be recovered by back-extraction into, say, 10 ml of N-sodium hydroxide, and could then, if desired, be titrated in a much smaller volume. In general, since traces of copper and iron would accompany zinc, whether or not the solvent extraction were used, titrations with ethylenediaminetetra-acetate would be performed in solutions where masking with cyanide had been carried out. It was proposed to neutralise the acid eluates from resin columns with

sodium hydroxide solution, rather than with ammonia, which would lead to a somewhat high concentration of ammonium salts which might cause difficulty (106), and then to buffer to between pH 9 and 10 with ammonia and ammonium chloride; or to add to the alkaline extracts from the solvent extraction procedure sufficient solid ammonium chloride to bring the pH within that range. Experiments were carried out with different compositions of solutions in order to find out what, if any, effect was caused thereby.

TITRATION IN SIMPLE BUFFERED SOLUTIONS

A series of experiments were performed in order to examine the titration of different amounts of zinc with a 0·02 M solution of disodium ethylenediaminetetra-acetate. Titrations were performed in a volume of ca. 100 ml of solution, buffered at a pH of about 10 with ammonia and ammonium chloride, containing solochrome black as indicator (~50 mg of a 1:200 w/w mixture with sodium chloride), the reagent being added until no further change of the indicator colour towards blue occurred. The end-points were in all cases sharp and distinct. The results obtained indicate that the consumption of ethylenediaminetetra-acetate is proportional to the weight of zinc taken.

Zinc taken, µg = X	6102	5939	5241	4413	3308	1943	1014	585	497
Vol. of E.D.T.A., ml = Y (corr. for blank)	4·775	4·620	4·080	3·430	2·580	1·505	0·780	0·445	0·375
X/Y, µg/ml	1278	1286	1284	1286	1282	1291	1300	1310	1320

Blank = 0·02 ml of E.D.T.A. solution, = 25 µg of zinc.

Since the results for small amounts of zinc were liable to be inaccurate when such small volumes of titrant were delivered

from an ordinary 10-ml burette, a change was made to a 0·004 M ethylenediaminetetra-acetate solution, and a similar series of experiments were carried out with this solution, with the following results.

Zinc taken, μg = X	2289	2428	2396	2445	2325	609	522	225	226
Vol. of E.D.T.A., ml = Y (corr. for blank)	7·73	8·12	8·06	8·24	7·82	2·05	1·75	0·76	0·76
X/Y, μg/ml	296	299	297	297	297	297	299	296	298

Blank = 0·01 ml of E.D.T.A. solution = 3 μg of zinc.

Variation of the volume of the solution titrated from 25 to 250 ml did not influence the results, although the end-points were somewhat less easily distinguished when the volume was small.

While the precision of the results obtained on any one day was generally good, slight fluctuations in the 'factors' for the various ethylenediaminetetra-acetate solutions employed, greater than could be attributed to experimental error, were noticed, and standardisation of the titrant solutions was therefore required daily. Such fluctuations were later found to be apparently connected with the use of Jena glass bottles for the storage of the solutions, as on changing to polythene containers steady 'factors' were obtained. There is no obvious explanation of this phenomenon.

TITRATIONS IN SOLUTIONS TREATED WITH CYANIDE AND AN ALDEHYDE

As 5 mg was the nominal upper limit to the amounts of zinc being considered, it was decided that cyanide sufficient to complex ca. 10 mg of zinc should safely cover all requirements. 1 Ml of a 5 % w/v solution of potassium cyanide was therefore used. For the liberation of the zinc from the cyanide complex, both formaldehyde and chloral hydrate have been suggested. Kinmunen and Merikanto (107) were the first to describe a procedure of this type, with formaldehyde, which has also been used by Flaschka (98) and by Brown and Hayes (78). Chloral hydrate was originally suggested for use by Přibil (108) and has been used little by other workers. In the early experiments of this investigation, both demasking agents were examined, but as formaldehyde polymerised and contained some impurity which had to be removed by dithizone extraction, chloral hydrate was eventually selected for exclusive use. 1 Ml of a 50 % w/v solution was found to completely demask zinc complexed by the specified amount of cyanide. With 5 mg of zinc, the indicator colour became pink within a few seconds of the addition of the demasking agent, but with small amounts, and blanks, the colour change from blue to pink was slower, and sometimes incomplete. Portionwise addition of the demasking agent offered no advantage in the titration of small amounts of zinc, although it is said to improve results with large amounts (63), and a constant amount of the demasking agent was therefore employed.

Titrations were carried out with various amounts of zinc in solutions approximating to those likely to be obtained after application of a solvent extraction procedure. The initially acid solutions were neutralised with 2 N-sodium hydroxide, with

the addition of 5 ml in excess, then treated with 0·8 g of solid ammonium chloride, potassium cyanide, indicator, and chloral hydrate, in the stated quantities. The solutions were blue before the addition of the chloral hydrate and required no titration at that stage. As for buffered solutions without cyanide etc., it was found that the end-points were more distinct if the titrations were carried out in volumes of ~100 ml than in ~25 ml. All, however, were much less sharp than those obtained in the simple buffered solutions; the colour change commenced about 1 ml of 0·004 M-ethylenediaminetetra-acetate before the end-point in titrations with zinc present, and was almost indiscernible in blank experiments. In an attempt to overcome this difficulty, a screened indicator solution was prepared, containing solochrome black, naphthol yellow-S and o-cresolphthalein. With this solution, the colour change on titration of a solution containing zinc was from red-orange via a neutral grey-brown to a bright green, and the grey-brown stage was taken as the end-point (cf. Debney (50)). As the indicator solution was not very stable and considerable uncertainty persisted in detecting end-points, especially in blanks, its use was soon abandoned, and a return made to the use of unscreened solochrome black, which, from now onwards, was used mostly as a 0·1 % solution in pyridine. This solution is reasonably stable, and, while the smell is somewhat unpleasant, it is superior to the solution in triethanolamine which has been recommended (109), in so far as its lower viscosity makes its measurement much simpler. Later work on spectrophotometric titrations showed that the use of the grey-brown 'end-point' with the mixed indicator was not justifiable.

Various results are shown in Table XV. Although the blank is frequently recorded as 0, the colour of the solutions in such blank experiments after the addition of chloral hydrate was not pure blue. Addition of ethylenediaminetetra-acetate caused an increase in 'blueness', but this change was so gradual that no end-point in the titration could be distinguished. The 'Zinc found' results are calculated from standardisations of the reagent solution with zinc in simple buffered solutions.

TABLE XV

Zinc taken µg	Zinc found µg	Error µg	Blank µg Zn
6151	6194	+43	0
5471	5511	+40	
2369	2372	+3	33
2337	2363	+26	
2208	2248	+40	0
2200	2236	+36	
748	818	+70	10
731	792	+61	
670	751	+81	0
535	600	+65	
258	316	+58	0
329	395	+66	

The errors are seen to be all positive, the worst being associated with the smaller amounts of zinc, and especially with the 0 blanks. In some of the titrations a certain slowness in the reaction was observed as the end-point was approached. There was evidently some effect due to the use of cyanide and chloral hydrate which gave inaccurate results. The errors suggested that undertitration of the blank was probably the main source of the trouble, and steps were taken to minimise the blank by distilling

the acids used and employing deionised water where practicable. Even with these precautions, considerable irregularities were still encountered, and it was found that large blanks were generally associated with poorer end-points in the corresponding zinc titrations, which suggested that a variable impurity effect was involved.

In tentative experiments with zinc alone, where anion exchange or solvent extraction or both operations had preceded titration, and where potassium cyanide and chloral hydrate were used, the end-points in all experiments, including the blanks, were sharper than in direct titrations in such solutions, although not as sharp as for standardisations in simple buffered solutions. This suggested that the difficulty with the end-points was perhaps partly associated with the presence of an impurity which was removed by ion exchange or solvent extraction. The presence of a trace of iron or other impurity which blocked the indicator in the sodium hydroxide solution was revealed in a separate experiment. About 5 ml of the alkali solution was the maximum amount tolerable in a direct titration experiment if serious difficulty was not to be encountered, although if the solution for titration was collected from an anion-exchange column it seemed possible to use more. However, even if ammonia were substituted for the sodium hydroxide entirely, trouble was still found and poor results were still obtained.

Because of the discrepancies between results for titrations, especially of small amounts of zinc, in simple ammonia-ammonium chloride buffered solutions and in solutions treated with cyanide and chloral hydrate, it was decided that in experiments involving the separation of zinc from other elements before titration, the

ethylenediaminetetra-acetate solutions used would have to be standardised with similar amounts of zinc contained in solutions of approximately the composition of those for the final titration. However, when this was done, it was frequently found that the results obtained in tentative experiments on the determination of zinc separated by anion exchange and/or solvent extraction were less accurate than if the standardisation of the ethylenediaminetetra-acetate were based on titrations in simple buffered solutions. It was impossible to decide whether or not the recovery of zinc was quantitative.

The Use of Ascorbic Acid for the Reduction of Iron (III)—

At this stage attention was drawn to the possibility of reducing iron (III) to iron (II), even in the presence of some nitric acid, by means of ascorbic acid (110). The method, as applicable in determinations of various elements with ethylenediaminetetra-acetate, has since been described by Flaschka and Püschel (111). When use was made of this reagent in a slightly acid solution, followed by buffering at pH ~10 and warming with potassium cyanide to complex the iron as ferrocyanide, and then, after cooling, the zinc was liberated by chloral hydrate and titrated as usual, a marked improvement in the end-points, especially in blanks, resulted. The colour change was still spread over a fair range of volume of titrant before the end-point was reached (cf. p. 84), but the actual end-point was more definite, the final colour being more purely blue than previously. This suggested that the difficulty with the end-points had, at any rate in part, been due to iron (III).

With this means of dealing with the problem of iron , the need for solvent extraction of zinc pyridine thiocyanate was

distinctly diminished, and the general direct application of the titration to the effluents from the resin columns was considered. The following outline procedure was accordingly devised.

To the eluate add 2 N-sodium hydroxide until neutral to metanil yellow (pH ~2 - 3), reduce the iron, including any introduced with the alkali, with ascorbic acid, complete the neutralisation with ammonia, buffer to pH 10 and add potassium cyanide. Heat to ca. 70°C for 10 minutes to form ferrocyanide, cool, add solochrome black indicator, titrate if necessary, then add chloral hydrate and titrate the liberated zinc. Some tartrate should generally be added before the final neutralisation to obviate the precipitation of iron (II) hydroxide etc.

Series of experiments with different amounts of zinc, some initially in solutions containing hydrochloric, hydriodic and nitric acids, in which case ascorbic acid was also used for the reduction of the free iodine, were performed by the above procedure, giving the results shown in Table XVI.

TABLE XVI

Zinc taken µg	Zinc found (corrected) µg	Error µg	Blank µg Zn
5022	5036	+14	8
5172	5190	+18	
4767	4787	+20	10
4855	4882	+27	
1926	1944	+18	8
1818	1836	+18	
600	604	+4	8
633	642	+9	

by titration in presence of 0·5 mg of zinc, and subsequent deduction of this amount, the blank was found to be only 29 ± 2 μg of zinc. This showed that the value used for the blank as obtained by direct titration was obviously not truly applicable in the presence of zinc, although the correction required might not be as much as 53 μg, as passage of the zinc through the resin in a normal experiment might have some influence.

Even with the use of ascorbic acid, the end-points with cyanide and chloral hydrate used were still not as sharp as was desirable, and it was accordingly decided to try to examine spectrophotometrically the various types of end-points obtained in titrations under the different conditions, in an attempt to find a means of improving the accuracy of the results.

SPECTROPHOTOMETRIC TITRATION EXPERIMENTS.

The use of a spectroscope to facilitate the detection of the end-points in certain difficult titrations was suggested by Tingle (112). Various photoelectric devices, used in conjunction with coloured filters were later applied to such problems (113). The development of the spectrophotometer, combining spectroscope and photometer in one instrument, caused further advances in such techniques. Recently, several procedures for spectrophotometric titrations with complexing agents have been described, which may be divided into two classes: those in which no indicator is added and the absorption of radiation of selected wavelength by the reaction mixture is examined; and those in which the colour change of an added indicator is followed spectrophotometrically. The first of these classes includes

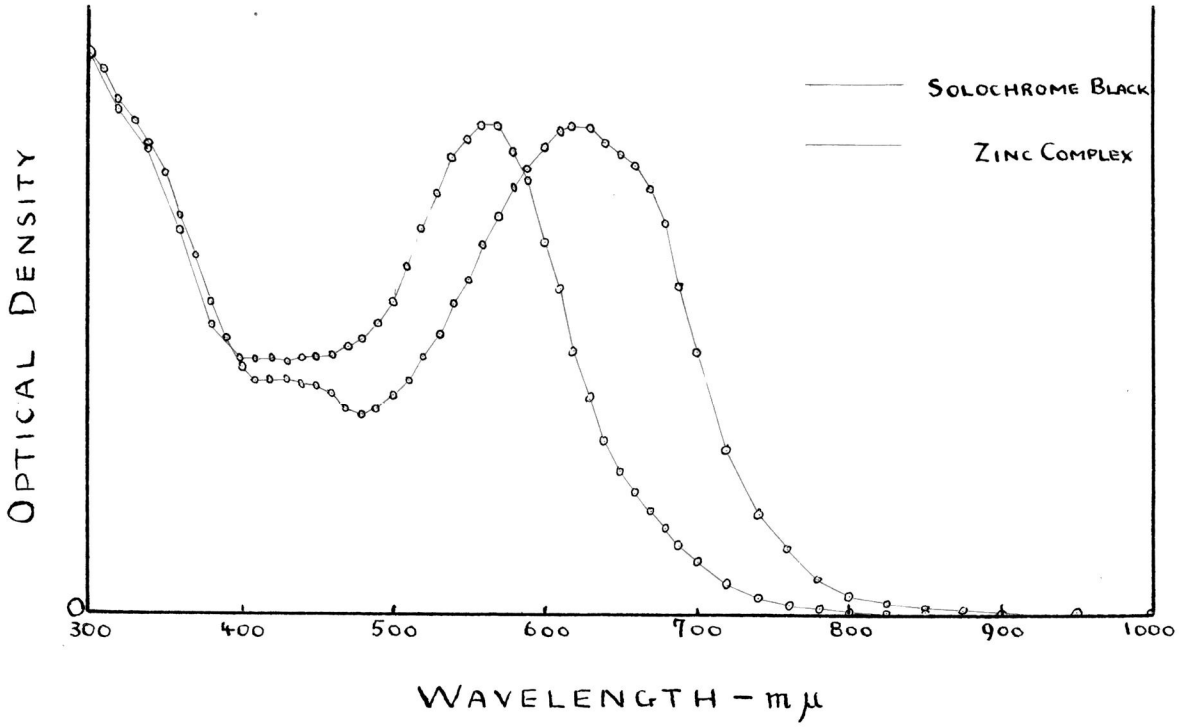


FIGURE 4

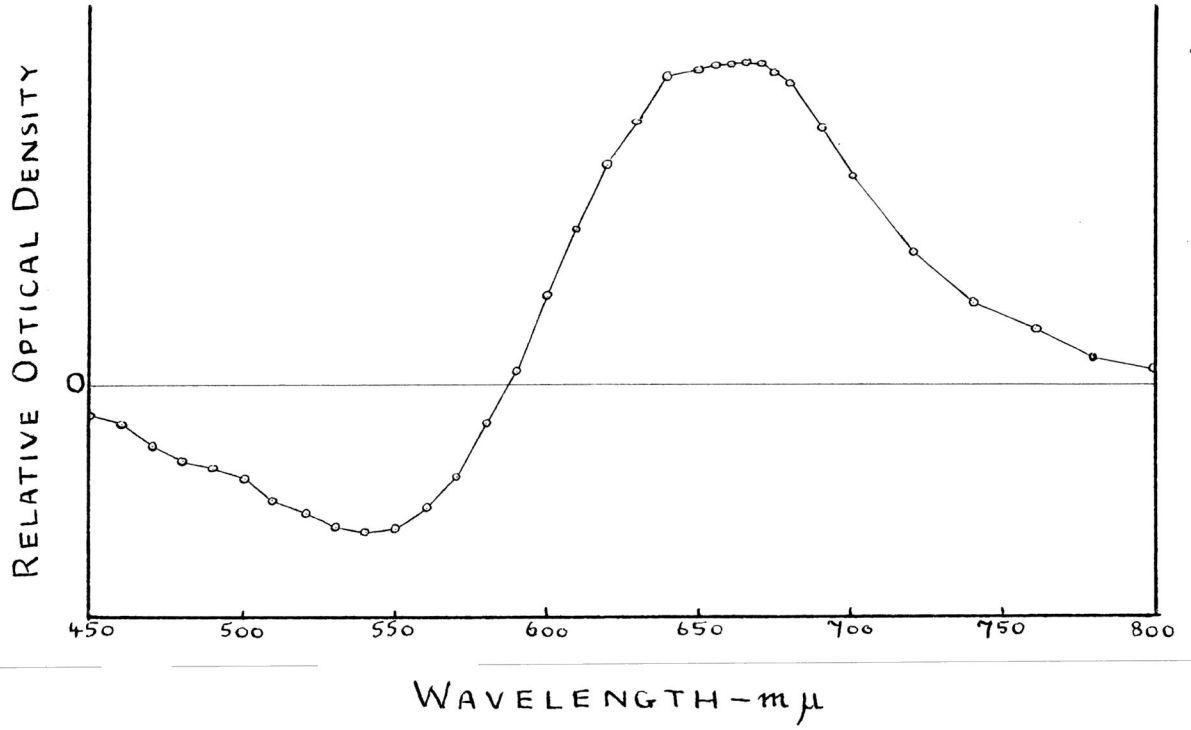
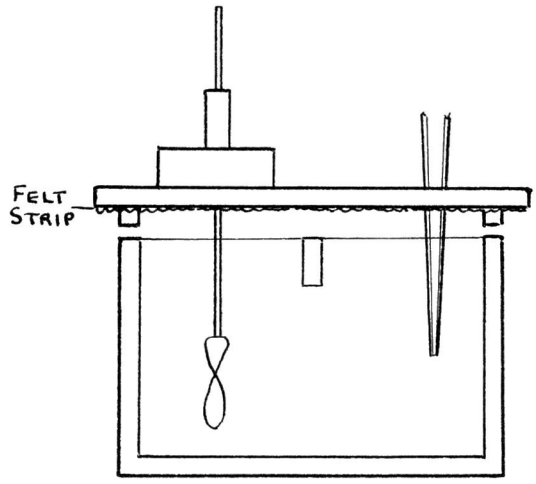


FIGURE 5

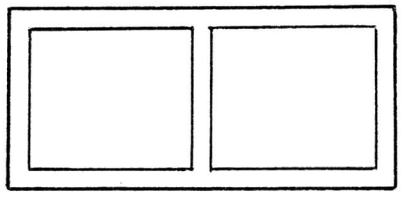
the procedures described by Sweetser and Bricker (103,114) for the determination of copper, nickel, magnesium, calcium, cadmium, and zinc. Examples of the latter class, where an indicator is employed, are found in these authors' work on iron and titanium, and in the micro-titration of calcium with disodium ethylene-diaminetetra-acetate described by Chalmers (115). The theoretical treatment of the end-point detection in such titrations has been given by Fortuin, Karsten and Kies (116), and Karsten and co-workers have examined the behaviour of several titrations with a number of indicators under various conditions (117).

Both types of spectrophotometric titration were considered in connection with zinc and ethylenediaminetetra-acetate. The method of Sweetser and Bricker (103) was successfully applied to zinc in ammonia-ammonium chloride buffered solutions, working at a wavelength of 225 mμ. However, on attempting to titrate zinc in this manner in a solution which had been treated with potassium cyanide and chloral hydrate, the solution was found to be essentially opaque at wavelengths under 300 mμ. Replacement of the chloral hydrate by formaldehyde or acetaldehyde effected no improvement.

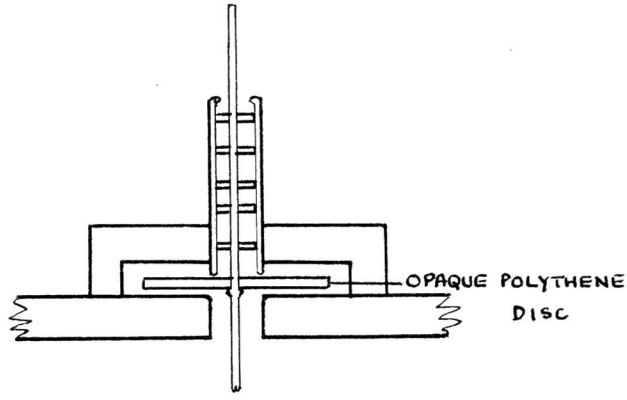
The spectrophotometric titration of zinc in the presence of solochrome black was therefore examined. The absorption spectra of solochrome black and of its zinc complex, in equal concentrations in ammonia-ammonium chloride buffers of pH 10, were measured over the range 300 to 1000 mμ. These are shown in Fig. 4, and it is apparent that the greatest differences are in the visible region, especially about 550 and 650 mμ. In Fig. 5 is shown the relative optical density of the solution of the zinc complex compared with the solution of the free



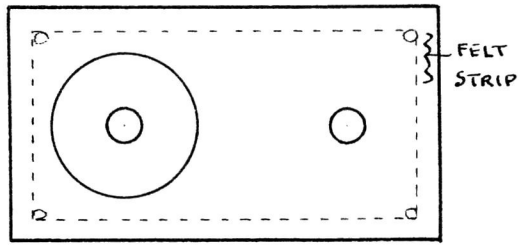
ELEVATION (× ½)



PLAN OF CELL (× ½)



STIRRER ASSEMBLY (× 1)



PLAN OF COVER (× ½)

FIGURE 6

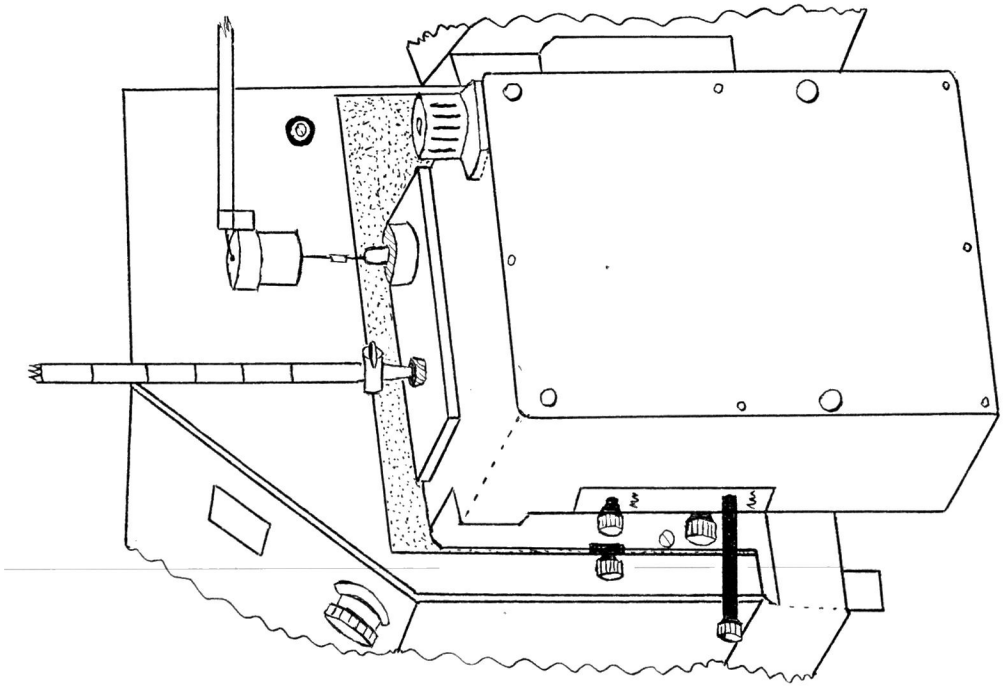


FIGURE 7

indicator at different wavelengths. The ordinate function is $\log \frac{I_{t(Zn-C)}}{I_{t(S.B.)}}$ where $I_{t(Zn-C)}$ and $I_{t(S.B.)}$ are the intensities of the light passing through the solutions of the zinc-solochrome complex and of the free indicator respectively, the source intensity being the same in both cases. The maximum value of the absolute value of this function occurs at 665 mμ, and this wavelength was therefore selected for use in experiments. It is apparent that over the range from 640 to 675 mμ there is little change in the relative optical density, and a sufficiently sensitive filter photometer with a filter transmitting this waveband could presumably be used.

Some exploratory experiments indicated that end-points could now be obtained for titrations of zinc with ethylenediaminetetra-acetate, even in the presence of cyanide and chloral hydrate. A special cell was therefore constructed of 'Perspex' (polymethylmethacrylate) sheet, designed to occupy the whole of the cell compartment of a Unicam SP 500 spectrophotometer (Fig. 6), together with a suitable cover through which a burette and stirrer could be introduced. The cover was rendered light-proof by coating the Perspex with opaque paper; chloroform was a satisfactory adhesive. The complete assembly as used is shown in Fig. 7.

Since at the selected wavelength (665 mμ) the absorption of light by the free indicator was greater than for the zinc complex, the initial setting of the spectrophotometer was performed with the untitrated solution as if this were the solvent, to give an optical density of '0'. During the titration, the ethylenediaminetetra-acetate solution was added in suitable increments, and, after mixing, the new value of the

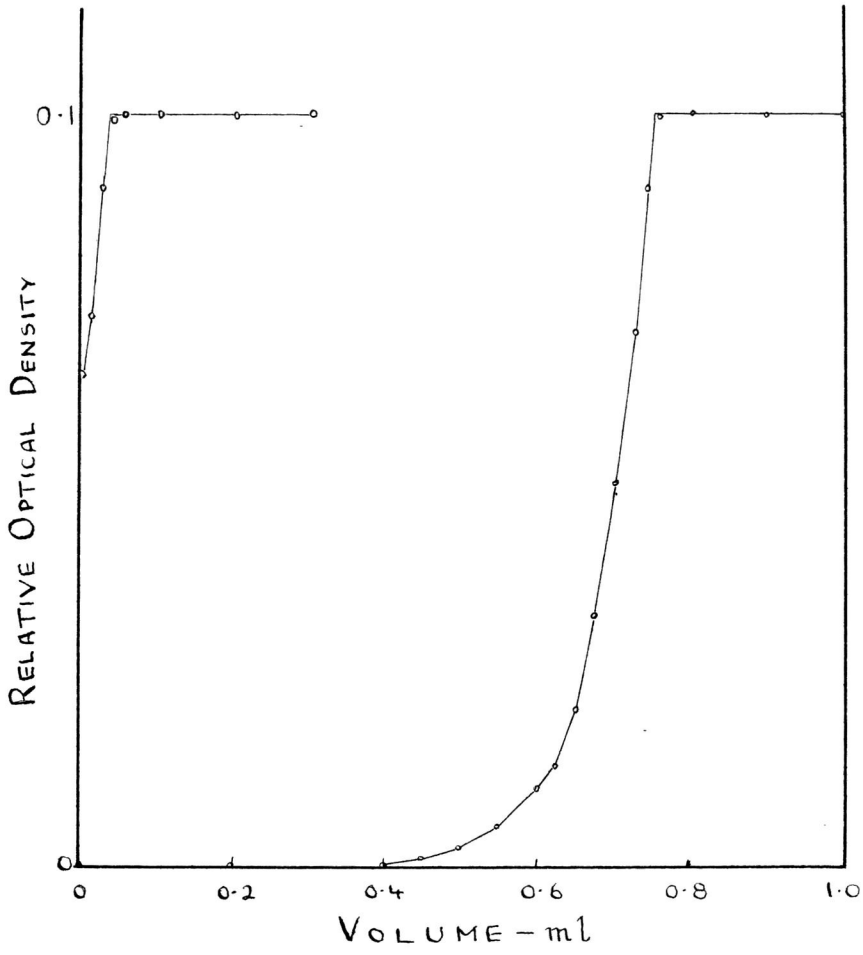


FIGURE 8

optical density was determined. The graph of optical density reading vs. volume of titrant added was then drawn and the volume corresponding to the end-point break in the curve determined.

From theoretical considerations (116) it is recommended that the amount of indicator used be kept small. A change in optical density of 0·1 during a titration was considered likely to be adequate for easy location of the end-point. Since it was easiest to use the indicator in solution, a pyridine solution was prepared as follows. 0·2 G of solochrome black (B.D.H.) was extracted with several 10-ml portions of warm (40°C), carefully purified pyridine until no further extraction of coloured matter was occurring. About 50 % of the dyestuff dissolved. The solution was filtered and diluted with pyridine to 100 ml. Such solutions, stored in stoppered Pyrex glass bottles, showed little deterioration during about 3 months of use. After this time, about 10 % of the indicator was found to have been inactivated, probably as a result of absorption of atmospheric moisture by the solution, and the solution was then renewed. For titrations in a volume of ca. 100 ml, 0·1 ml of indicator solution was found to give a suitable change in optical density, of ca. 0·1. With blanks, the change in optical density was generally less than this, and as little as 0·004 was sometimes encountered.

For titrations in simple ammonia-ammonium chloride buffered solutions, the graphs of optical density vs. volume were of the form shown in Fig. 8, very sharp end-points being obtained with as little as 50 µg of zinc present. The end-point sections of the curves were virtually identical for all amounts of zinc. Those shown are for the titration of a blank and of ca. 100 µg

FIGURE 9

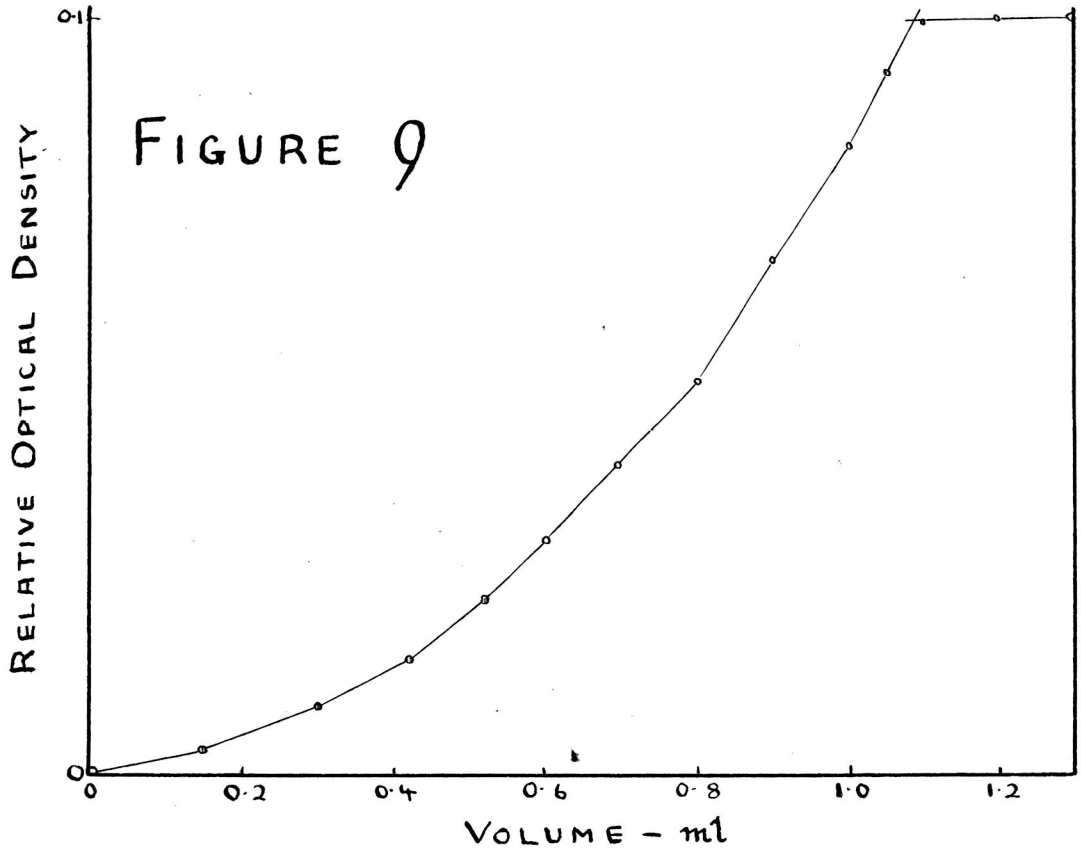
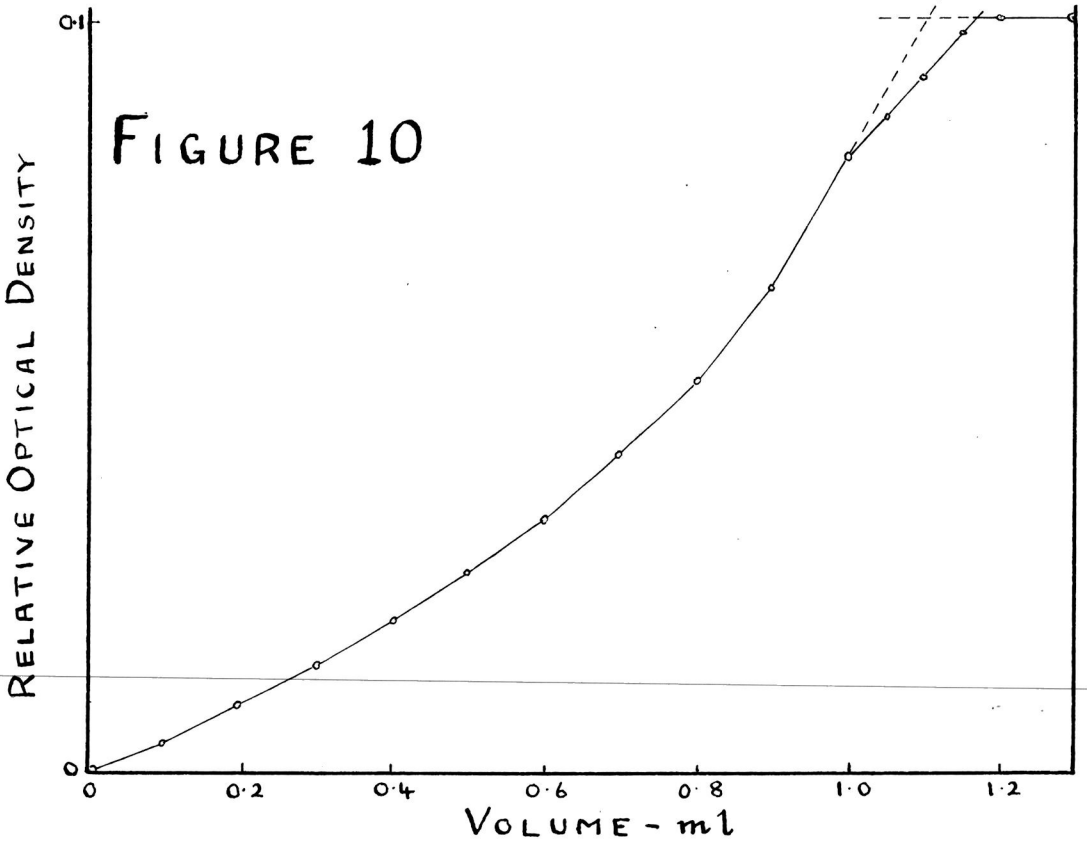


FIGURE 10



of zinc. In such titrations, the 'factor' for the ethylene-diaminetetra-acetate solution was found to be independent of the amount of zinc taken (cf. p. 82). This is shown in the following results:

Zinc taken, µg = X	9961	924	554	128	0
Vol. of E.D.T.A., ml = Y (corr. for blank)	59·30	5·50	3·30	0·77	0·02ml = 3 µg Zn
X/Y, µg/ml	168·0	168	168	166	-

On addition of cyanide and chloral hydrate to such solutions, the titration curves, while still showing sharp end-point breaks, rose less steeply, as shown in Fig. 9, which is a typical curve for the titration of 100 µg of zinc. It was obvious that this explained the greater uncertainty in locating the end-points visually in solutions to which cyanide and chloral hydrate had been added.

With solutions to which sodium hydroxide and ascorbic acid had been added as well as cyanide and chloral hydrate, the titration curves showed similar flattening as compared with those for simple buffered solutions, and also rounding of the end-point break (Fig. 10). Two extreme end-point values can be distinguished, but the actual end-point is uncertain. This rounding of the end-point break in the curves was obviously the spectrophotometric counterpart of the uncertain visual end-points encountered in similar titrations. The results deduced for small amounts of zinc were generally low with respect to standardisation of the titrant against zinc by titration in simple buffered solutions, whether the first 'end-point', derived by projection from the inflexion, or the second was used for calculation, the same one being, of course, selected for the determination

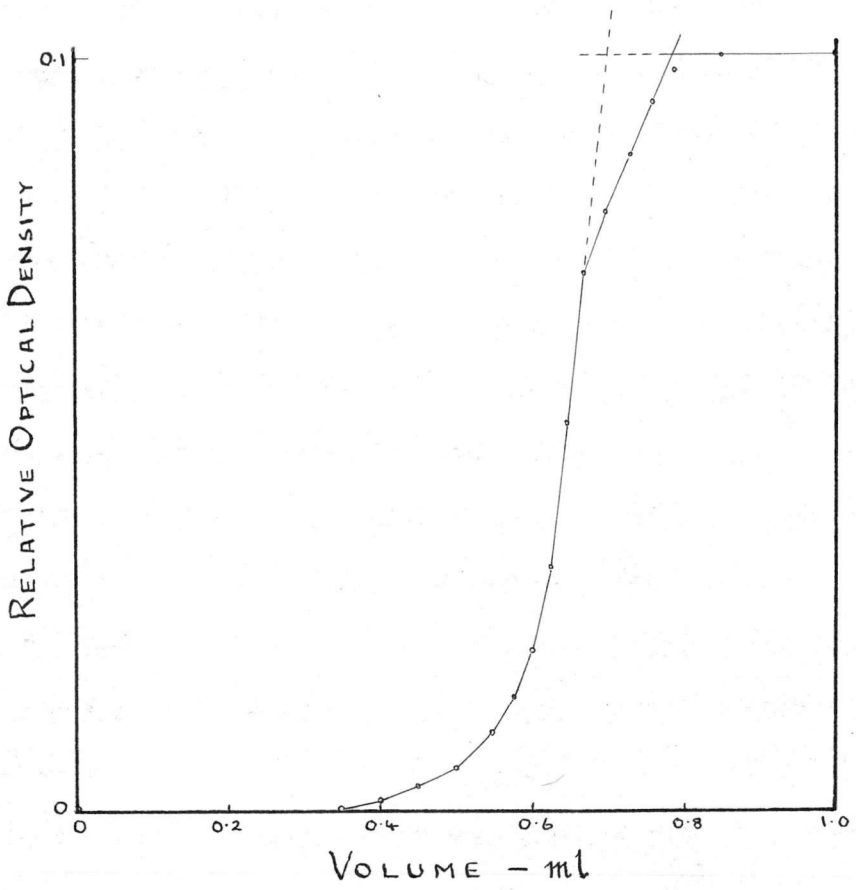


FIGURE 11

of the blank. There was evidence of the presence of impurity as the change in optical density was sometimes less than normal. This could not be iron^{III}, as ascorbic acid had been used.

In an experiment where 2 g of sodium chloride were added to an ammonia-ammonium chloride buffered solution containing zinc, the titration curve was of the form shown in Fig. 11. The initial rise was steep, as in the absence of sodium chloride, but the double end-point phenomenon was again encountered. A similar result was obtained with a different sample of sodium chloride. Přibil (106) says that the interference of sodium ion in titrations where solochrome black is used as indicator is negligible, so that an impurity is perhaps more likely to be the cause of the difficulty. It was therefore desirable to find out whether satisfactory results could be obtained when pure ammonia was used for neutralisation, and sodium hydroxide and sodium chloride were excluded. A series of experiments, in sets of two determinations of ca. 100 µg of zinc and a blank, were carried out under various conditions, and all gave similar good results as shown in Table XVIII. The results are calculated on the basis of standardisations of the ethylenediaminetetra-acetate solution by spectrophotometric titration in ammonia-ammonium chloride buffered solution - cf. p.107.

TABLE XVIII

	Zinc taken µg	Blank µg	Error µg	Procedural Notes
A	121 130	7	-3 0	Solution containing 5 ml of 2 N-HCl treated with 5 N-NH_4OH till neutral + 2 ml in excess - diluted to 100 ml.
B	126 123	7	0 +4	As set A with additional 1 g NH_4Cl
C	117 71	20	-3 0	As set B with treatment with cyanide and chloral hydrate
D	92 67	13	+5 +1	Solution containing 5 ml 2 N-HCl, 5 ml 2 N-HI, 60 ml 0·25 N-HNO_3, decolorised with ascorbic acid, neutralised with 5 N-NH_4OH + 2 ml in excess, → 100 ml.
E	95 100	26	+2 +3	As set D with treatment with cyanide and chloral hydrate.

These results suggested that if pure ammonia were used to neutralise the acid eluates from anion-exchange columns, and an excess added to raise the pH to 9·5 to 10, spectrophotometric titrations could give good results, even for amounts of zinc as small as 100 µg.

A series of experiments with amounts of zinc ranging from 0·1 to 10 mg, initially in hydrochloric - hydriodic - nitric acid solution was carried out, with treatment as in set E in Table XVIII, with the following results.

Zinc taken, µg	10010	4829	2340	920	489	115	0
Vol. of E.D.T.A., ml (corr. for blank)	64·02	30·89	14·96	5·91	3·14	0·75	0·35 (≡54 µg)
'Factor', µg/ml	156·4	156·3	156·4	155·7 ± 0·3	156·2 ± 0·5	153 ± 3	
Error, µg (Based on 'factor' of 156·3)		-3	0	-2	+4	+1	+2

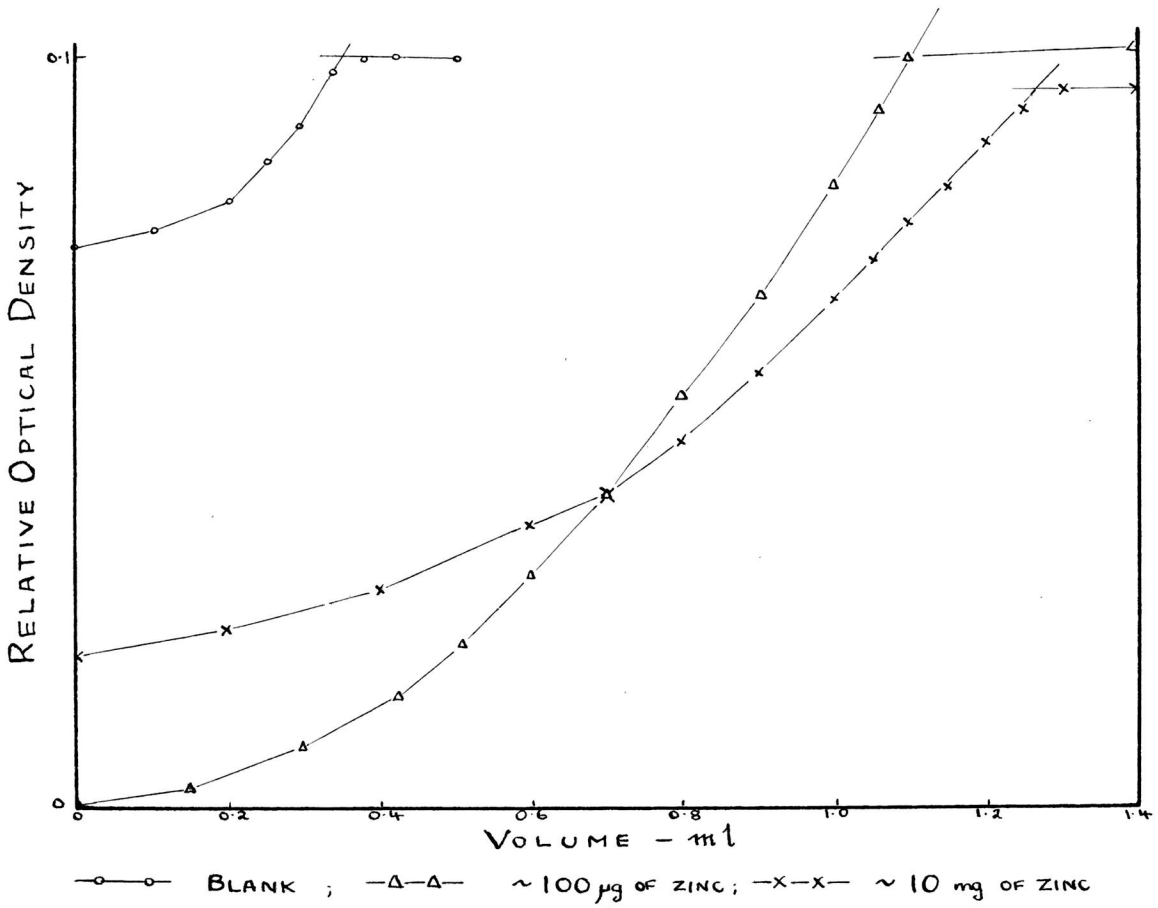

RELATIVE OPTICAL DENSITY
0·1
0
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
VOLUME - ml
—o—o— BLANK ; —Δ—Δ— ~100 μg OF ZINC ; —X—X— ~10 mg OF ZINC

FIGURE 12

The 'factor' is seen to be essentially constant.

While the end-points in titrations in such solutions are distinct, they are not as sharp as those obtained in titrations in simple ammonia-ammonium chloride buffers. This effect is not due to slowness of reaction, and suggests the occurrence of competitive complexing of the zinc, possibly by the chloral-cyanhydrinyl ion. In titrations where the full range of optical density (0 to 0·1) is covered, this causes no difficulty: the end-points can be determined with an accuracy of ± 0·005 ml of 0·0025 M-ethylenediaminetetra-acetate solution. With blanks the uncertainty is greater, and may occasionally reach 0·025 ml, the equivalent of 4 μg of zinc. This is mainly due to the titration curves for blanks not corresponding to the final stages in titrations with zinc present, but being sometimes considerably less steep. In Fig. 12 are shown titration curves for the blank and for the first and last titrations in the series of experiments described at the foot of p. 96. The blank is seen to give the flattest curve, and the curve for the titration of ~100 μg of zinc is seen to be somewhat steeper than that for ~10 mg, (of which only the end part is shown). On occasions, much flatter titration curves were encountered with blanks. Any uncertainty in the blank will not in general influence the precision of a set of experiments, unless the amounts of zinc differ considerably, but the accuracy will be diminished.

In almost all experiments, the optical density reading has remained steady in the 'plateau' region after the end-point, although occasionally a slight slope up or down has been observed. Very occasionally no end-point has been detected because of 'blocking' of the indicator by adventitious impurity.

With reference to Fig. 12, it is apparent that the error which would be introduced if the volume reading corresponding to half change of the indicator ('optical density' ~0·05) were taken as the end-point would be different for different amounts of zinc. This is the spectrophotometric counterpart of the use of the screened indicator for visual titrations as previously described (p. 84) and it is therefore obvious that such a procedure will not give correct results. A similar argument would hold against titration of the zinc-containing solution to match the colour of an untitrated blank; full titration of all solutions is the only reliable method.

Since in the results for the tentative ion-exchange experiments with visual titration (p. 89) there had been evidence that the value obtained by direct titration of the blank was incorrect, it was necessary to find whether the blank determined by spectrophotometric titration was applicable in experiments where this technique was used. A series of experiments, along the lines used for the visual titration sets previously described, were carried out with spectrophotometric titration, and the following results were obtained.

Blank by resin procedure 'A' (p. 53) determined directly	45 ± 3 µg
Blank by resin procedure 'A' determined after addition of 120 µg of zinc	47 ± 5 µg
Blank by resin procedure 'A' determined after addition of 600 µg of zinc	42 ± 1 µg

There is seen to be no important discrepancy between the values obtained directly and by deduction of a known amount of added zinc.

A few experiments with 0·5- and 5-mg amounts of zinc carried through the ion-exchange procedures 'A' and 'C' (pp. 53 and 71, respectively) gave satisfactory results on spectrophotometric titration, as shown in Table XIX.

TABLE XIX

Procedure on resin	Zinc taken (approx.) mg	Error µg	Blank µg Zn
A	5	-17 -24	49
	0·5	0 -5	27
C	5	+2 -12	55
	0·5	+1 +10	53

The results, especially for the small amounts of zinc, are seen to be superior to those obtained in the visual titration experiments and recorded in Table XVII, p. 89.

The Influence of Other Elements —— Since spectrophotometric titration was obviously capable of giving more accurate results for the determination of zinc than visual titration, especially in solutions which had been treated with cyanide and chloral hydrate, it was now possible to study with confidence the separation of small amounts of zinc from other elements by anion exchange. From the data given in Table XIV, p. 76, the following elements, in various small amounts, might be expected to be present along with the zinc after such separations, and their effects on the titration required examination: antimony^{V}, copper^{II}, gallium, germanium, indium, iron^{III}, lead, manganese^{II}, molybdenum^{VI},

platinum^{IV}, tellurium^{IV}, thallium^{I}, thorium, tin^{IV}, titanium^{IV}, tungsten^{VI}, uranium^{VI}, and zirconium.

Germanium was not considered further as volatilisation as the tetrachloride would serve for its removal. Antimony was not expected to interfere if tartrate were added to prevent precipitation (98) and the small amount (ca. 500 µg) coming from a column to which 50 mg of antimony^{V} had been applied prior to treatment by procedure 'B' (p. 66) caused no trouble in the determination of 500 µg of zinc. Experiments with ca. 350 µg amounts of zinc showed no interference to occur in presence of the following elements in the amounts quoted, when solutions initially containing hydrochloric, hydriodic, and nitric acids were treated with ascorbic acid, ammonia, cyanide, and chloral hydrate: copper^{II}, 500 µg; iron^{III}, 500 µg; molybdenum^{VI}, 10 mg; platinum^{IV}, 2·5 mg; thallium^{I}, 100 µg; thorium, 500 µg; tungsten^{VI}, 2·5 mg. Tellurium^{IV} was reduced to the elementary form by the ascorbic acid and might be removable as such. Half-milligram amounts of titanium and zirconium caused no interference if the titrations were performed rapidly after adding the indicator, but on standing a slow reaction occurred, especially with titanium, causing 'blocking' of the indicator. With uranium^{VI}, only a few micrograms were tolerable, even with rapid titration, if no interference was to be encountered. Titanium and uranium must therefore be considered as potentially interfering, as larger amounts than these might be encountered.

Manganese^{II} and lead were not complexed by the cyanide, and produced pink and purple colours, respectively, in the solutions, before the addition of the chloral hydrate, which could be changed to blue by adding ethylenediaminetetra-acetate. In the case of

manganese, it is necessary to have a slight excess of ascorbic acid present to prevent oxidation to manganese(III), which oxidises and destroys the indicator (118). No difficulty was encountered in the direct spectrophotometric titration of manganese^{II} in the cyanide solutions with ethylenediaminetetra-acetate, but for reasons to be discussed in connection with the titration of lead, addition of an excess of the reagent and back-titration has certain advantages, especially for the determination of the smallest amounts of zinc, and for blanks.

When ca. 1 mg of lead was present in a solution containing cyanide, the purplish colour obtained on addition of solochrome black changed to blue on titration with ethylenediaminetetra-acetate, but in a spectrophotometric titration experiment it was found that the reaction in the vicinity of the end-point was so slow that it was necessary to wait for at least five minutes after each addition of the titrant before a steady reading was obtained. The end-point break in the titration curve was sharp, as in Fig.8, although the total change in the optical density at 665 mμ was smaller. An attempt to find a more suitable wavelength for the titration of lead was unsuccessful; the difference in absorption between the lead-solochrome complex and the free indicator was always small. The titration of lead in cyanide solutions was attempted along the lines indicated by Sweetser and Bricker (103) for titrations without an added indicator in the ultra-violet region, but the solutions were found to be opaque at wavelengths under 300 mμ.

The possibility of accelerating the change in optical density in the titrations was examined. Addition of an excess of ethylenediaminetetra-acetate and back-titration with magnesium,

and also the addition of some magnesium and the titration of lead and magnesium together, were tried, but the results were disappointing. The titration of lead and manganese(II) together was found to be slow, but on addition of an excess of ethylenediaminetetra-acetate to a solution containing lead, and subsequent back-titration with a solution of manganese(II) chloride, this titration was found to be reasonably rapid, although a certain sluggishness made it advisable that the excess of ethylenediaminetetra-acetate to be back-titrated should be small. It was found that if ca. 100 µg of manganese(II) were added to the solutions containing lead, preferably before heating to convert any iron(II) present to ferrocyanide, a sharp colour change was afterwards obtained on addition of the indicator and titration with ethylenediaminetetra-acetate, which enabled the excess to be controlled visually to about 0·2 ml of a 0·0025 M solution. If the manganese were added after the indicator, partial 'blocking', probably by traces of manganese(III) occurred. The excess of ethylenediaminetetra-acetate could be readily back-titrated spectrophotometrically with a standardised 0·001 M-manganese(II) chloride solution, and the necessary excess of the latter, together with the zinc liberated by the chloral hydrate, titrated subsequently with ethylenediaminetetra-acetate. This procedure will be referred to as 'triple titration'. Some results for the determination of zinc in presence of 1 - 2 mg of lead, which were obtained by this means, follow. They have been corrected for the amount of zinc found in a control experiment with the same amount of lead carried through the whole procedure. This correction was of 40 µg of zinc.

Zinc taken, µg	5030	5144	464	533
Zinc found, µg	5063	5150	478	526
Error, µg	+33	+6	+14	-7

As stated on p.101, if titration of, say, manganese, is required at the cyanide stage, addition of an excess of ethylenediaminetetra-acetate and back-titration is preferable to direct titration. If direct titration is used, it may happen that the overshoot necessary for the establishment of the 'plateau' value of the optical density may also represent an excess with respect to the titration after liberation of the zinc by the chloral hydrate. Although back-titration here could, of course, be used, some uncertainty as to the direction of the titration required in a particular experiment might occur with an inexperienced operative which could cause confusion. Therefore, unless the amount of zinc present is known to be significant, and lead, whose slow reaction with ethylenediaminetetra-acetate makes 'triple titration' desirable, is known to be absent, the safest and simplest procedure when titration at the cyanide stage is required is the 'triple titration' as described herein.

Of the elements liable to accompany zinc from an anion-exchange column, the following remain as sources of potential interference: gallium, indium, tin[IV], titanium[IV] and uranium.[VI] Procedures for the titrations of the first two with ethylenediaminetetra-acetate have been described (119,120). For the titration of gallium, it is necessary to add an excess of the reagent and to back-titrate this with, for example, a standard lead solution. This procedure is necessary because of the weakness of the gallium-solochrome complex which does not form to a sufficient extent in solutions of pH 10 to serve as an

indicator. Even the gallium-ethylenediaminetetra-acetate complex is weak at this pH and titration at a lower pH is necessary for satisfactory results to be obtained. Gallium interfered in the titration of zinc but it was thought that the greater sensitivity of the spectrophotometric method might permit the titration of the gallium at the cyanide stage: but this was not found to be the case. The matter was not further investigated at this point as it was expected that gallium would be eliminated by solvent extraction of zinc pyridine thiocyanate. (cf. p.125). For the determination of indium, Flaschka and Amin (120) state that the solution for titration must be kept almost at the boiling-point, which cannot readily be done with the spectrophotometric titration technique, and which would be likely to cause trouble if tin were also present (vide infra). Indium must therefore be eliminated.

Tin did not seem to have much influence on the results obtained in visual titration experiments with zinc, but the end-point reaction was slow if much was present. By the spectrophotometric titration procedures, it was thought that the small amount of tin ($\leq$ 3mg) accompanying zinc from anion-exchange columns after treatment with methylarsonic acid would not cause much trouble. This expectation was not, however, fulfilled. In a series of experiments on the titration of zinc in the presence of tin, it was found that on heating the solutions, which contained 50 mg of tartaric acid, after addition of the potassium cyanide, in order to complex any iron(II) as ferrocyanide, hydrated stannic oxide precipitated out. On subsequent titration, without filtering off this precipitate, no zinc was found in an experiment where 300 µg had originally been present

in association with 5 mg of tin^{IV}. On examination of the precipitate after subsequent filtration, by ignition and dissolution in hydriodic acid, it was found, qualitatively, to contain the missing zinc.

Since the β-form of tin(IV) precipitates as the hydroxide even in the presence of tartrate, and since the change from the α- to the β-form is assisted by dilution of the solution,(121) it was suspected that this change was the most probable reason for the precipitation of tin and consequent loss of zinc. This was confirmed by the use of tin solutions of known form. With 5 mg of α-tin(IV), from a 10 % solution in 2 N-hydrochloric acid, no precipitate appeared on heating an ammoniacal tartrate solution at 40°C overnight, whereas with a similar amount of β-tin(IV), from a 1 % solution in 0·2 N-hydrochloric acid which had been allowed to stand for a few days, precipitation occurred readily on warming the ammoniacal tartrate solution. At a temperature of 40°C it was found that heating for ~15 minutes was adequate for formation of ferrocyanide from any iron(II) present (cf.p. 87). Precipitation of β-tin(IV) was not prevented by the addition of oxalate or citrate, or of more tartaric acid (200 mg), although the last effected some reduction in the amount precipitated, perhaps by retarding further conversion of α-tin to the β-form.

It was desirable to determine whether the tin eluted from an anion-exchange column was in the α- or the β-form. In an experiment where the effluent was immediately treated with tartrate etc., no precipitate was obtained, so that the eluted tin was evidently mostly in the α-form. Another experiment, where the eluate was fractionated, showed that most of the tin appeared during the period of washing with water, with some

more in the middle third of the nitric acid washings. It was therefore decided to place 1 ml of 25 % w/v ammonium tartrate solution in the flasks in which the zinc-tin eluates were to be collected and to carry out the subsequent operations as rapidly as possible, in order to minimise conversion of tin into the β-form.

By these means, the precipitation of stannic oxide was prevented, but an effect on the end-points in the titrations of zinc remained. This consisted in an overall flattening of the titration curves, the change in optical density being only about 0·03, although it occurred over the usual range of volume of titrant (Fig. 13). Visually, the change in colour was from lilac-grey to blue, and accurate visual titration would be very difficult. The presence of excess of ethylenediaminetetra-acetate was, however, detectable, and the visual first titration in the 'triple titration' procedure was still feasible if both tin and lead were present. It would, however, be advantageous if tin could be simply removed.

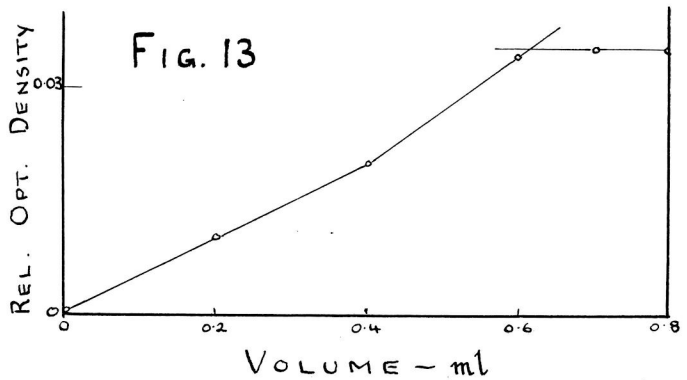


FIG. 13

From the foregoing remarks, it is evident that the determination of zinc with ethylenediaminetetra-acetate, after anion-exchange separations, would be simplified if certain interfering elements were removed before titration. Before describing the method whereby this has been to a great extent accomplished (p. 115 et seq.), the working procedural details of the various spectrophotometric titration techniques will be given.

DETAILED PROCEDURES FOR SPECTROPHOTOMETRIC TITRATIONS WITH A UNICAM S P 500 SPECTROPHOTOMETER

Standardisation of ca. 0·0025 M-disodium ethylenediaminetetra-acetate solution. — Switch on the spectrophotometer and lamp and allow to warm up, then adjust the 'dark current' to '0'. To a suitable aliquot of a standard zinc solution, containing ca. 5 ml of 2 N-hydrochloric acid, add 4 ml of 5 N-ammonium hydroxide, water to ca. 100 ml and 0·1 ml of the pyridine solution of the indicator prepared as described on p. 93. If the concentration of the reagent solution is not approximately known, titrate visually in order to ascertain the approximate position of the end-point (colour change from pink to blue) and prepare a fresh aliquot for the spectrophotometric titration. Transfer it to the titration cell (Fig. 6, p. 92*) with suitable washings, and place cell, cover, burette and stirrer in position on the spectrophotometer. Start the stirrer motor and adjust its speed so that the position of the galvanometer needle on the front of the instrument is not influenced by it, whether the dark current shutter be open or closed. With a wavelength of 665 mμ, balance the photometer bridge (switch at 'check') as is normally done with the solvent cell in position. Switch to '1'. Add the ethylenediaminetetra-acetate solution until 0·5 to 1 ml short of the end-point expected, and, after stirring for a short time, determine the value of the 'optical density'. Add the reagent in small measured increments (~0·1 ml), determining the 'optical density' after each addition, until a rapid change sets in, after which reduce the size of the increments to, say, 0·05 ml. After each addition, take two or more readings of the 'optical density' to ensure that equilibrium has been reached. Proceed

thus until no further change in the 'optical density' occurs, then add 0·5 ml of the ethylenediaminetetra-acetate solution to check that the 'plateau' reading has, in fact, been attained.

Draw the graph of 'optical density' against burette reading and from the 'edge' of the 'plateau', determine the burette reading at the end-point. Titrate a blank, containing all reagents, similarly, but add the reagent in small increments from the start. It is not generally worth while to balance the spectrophotometer again with the untitrated blank, although omission of this step may mean that the titration starts at an 'optical density' of, say, 0·075. This introduces no error, as only relative values are involved. During the titrations, any drift in dark current should be balanced out as required by the use of the 'dark current' control. Duplicate standardisations should be performed, and if the blank is not roughly known, it also should be duplicated.

Determination of zinc in the absence of lead, tin, indium, gallium, uranium, manganese, and titanium, as well as other metals removable by anion exchange (see Table XIV, p. 76) —— If anion exchange is used, the eluate containing the zinc should be collected in a flask containing 1 ml of 25 % w/v ammonium tartrate solution. Otherwise add to the solution, which may contain hydrochloric, nitric, and perhaps hydriodic acids, that amount of ammonium tartrate and proceed as follows. Add 0·1 ml of a fresh 1 % w/v solution of ascorbic acid in excess of what may be required to decolorise any iodine present, and then 5 N-ammonium hydroxide until neutral to methyl red plus 2 to 5 ml in excess (pH 9·5 - 10), or else until alkaline to thymol blue paper. Add

1 ml of 5 % w/v potassium cyanide solution and heat on a hot-plate to 70°C for 10 minutes or to 40°C for 20 minutes to form ferrocyanide from any iron(II) present. Cool in running water, and then add 0·1 ml of indicator solution. The colour here is expected to be blue. (If it is not blue, proceed as described in the following section). Add next 1 ml of 50 % w/v chloral hydrate solution and transfer, with washings, to the titration cell. Fit burette, stirrer, etc. as previously described and start stirring. Balance the spectrophotometer with the switch in the 'check' position. Switch to '1', set to an 'optical density' of 0·005 or 0·01, and with the dark-current shutter open, add the ethylenediaminetetra-acetate solution slowly, with stirring, until the galvanometer balances. Close the dark-current shutter and, after readjusting the dark current if necessary, proceed with the addition of the titrant in small increments as described for standardisation, making sure that the 'optical density' reading is steady after each addition. Carry out a similar titration on a blank which has been subjected to the full procedure. Determine the end-point as for the standardisation of the reagent.

If the amount of zinc is known to be large, much of the disodium ethylenediaminetetra-acetate may be added from a pipette (best calibrated in terms of the zinc equivalent of the reagent delivered) or a stronger solution (0·0075 M) may be used for much of the titration. The end-point should, however, be obtained by titration with an approximately 0·0025 M ethylene-diaminetetra-acetate solution.

The actual titration of an 'unknown' by the above procedure takes about seven minutes.

If it is desired to titrate zinc in the presence of tin^{IV}, the above procedure may be used, but care must be taken during the heating (20 minutes at 40°C) that no precipitation occurs, and the titration must be performed very cautiously, as the end-point reaction is somewhat slow and the change in optical density is only ca. 0·03 in most experiments. Small amounts of titanium (~500 μg) may be tolerated if the titration is carried out very rapidly after the addition of the indicator, but it is safer to eliminate it by solvent extraction - see p. 125.

Determination of zinc in the presence of lead and/or manganese - 'Triple Titration' —— If the initial solution is known to contain manganese, proceed as described in the preceding section, but with the addition of a further 0·25 ml of ascorbic acid solution. If lead is known to be present, add ca. 100 μg of manganese(II), as chloride, and 0·25 ml excess of ascorbic acid solution. Proceed as described in the preceding section until the indicator has been added, when the colour will not be blue, and add, very slowly, visually, a slight excess of ethylenediamine-tetra-acetate solution. The excess need not be known, but should, if possible, be not more than ~0·2 ml of 0·0025 M solution. Transfer the solution to the titration cell and assemble at the spectrophotometer as before, but with a burette containing a 0·001 M-manganese(II) chloride solution. Switch to '1', set to an 'optical density' of 0·1, and balance by means of the 'slit' and 'sensitivity' controls. Add the manganese solution slowly in small increments (~0·2 ml), determining the 'optical density' after each addition, until the reading starts to fall, and then decrease the size of the increments and increase the waiting period before reading in order to obtain true results. Do not

go further than necessary to locate the end-point. From the graph of 'optical density' vs. burette reading (cf. Fig. 14) determine the end-point and hence the excess of manganese(II) solution added.

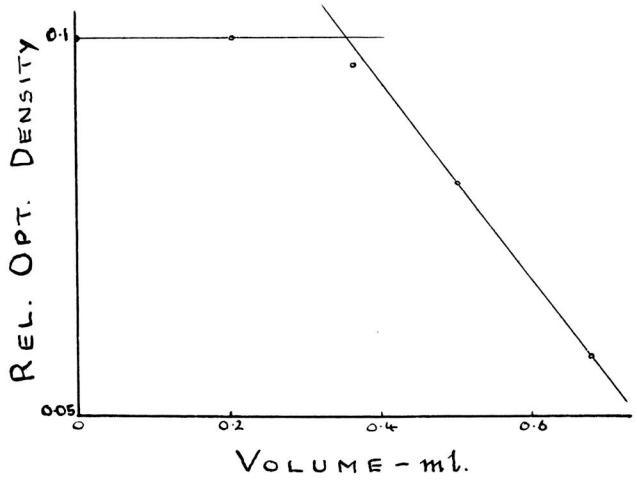


FIG. 14

Withdraw the burette, add to the solution 1 ml of chloral hydrate solution, rebalance the spectrophotometer, if necessary, with the switch at 'check', and then titrate with ethylenediaminetetra-acetate as previously described (p. 109). Deduct the disodium ethylenediaminetetra-acetate equivalent of the excess of manganese solution added from the volume consumed in this titration in order to obtain the volume equivalent to the zinc liberated by the chloral hydrate.

Standardise the manganese(II) chloride solution spectrophotometrically by adding a known excess of ethylenediaminetetra-acetate to a titrated blank (ammonia-ammonium chloride plus potassium cyanide) and back-titrating with the manganese solution.

A 'triple titration' requires about 30 minutes.

VISUAL TITRATION EXPERIMENTS - II.

Since spectrophotometric titration experiments had shown that the uncertainty of the end-points in experiments based on the cyanide - chloral procedure could be overcome by avoiding the use of sodium hydroxide, and, instead, employing ammonia for neutralising acids as well as for buffering, it was desirable to find out whether this change would yield a corresponding improvement in visual titration experiments, since the apparatus for spectrophotometric titrations would not be generally available. Some earlier visual experiments which had been performed with sodium ions excluded from the solutions had not given satisfactory results (p. 86). Various series of experiments were therefore carried out to determine whether precision, accuracy and proportionality of relationship between the ethylenediaminetetra-acetate and zinc were indeed improved. The reagent solution had been standardised by spectrophotometric titration, although the result for such a standardisation was the same as would be obtained by visual titration of a fairly large amount of zinc (2 - 5 mg) in a simple ammonia-ammonium chloride buffered solution.

A series of six experiments with *ca.* 1 mg of zinc, initially in solutions containing hydrochloric, hydriodic and nitric acids, and treated with ascorbic acid, ammonia, potassium cyanide and chloral hydrate, gave the following results.

Zinc taken, µg	1076	1311	1038	1340	1216	1105
Zinc found, µg (corrected)	1061	1322	1035	1339	1217	1106
Error, µg	-15	+11	-3	-1	+1	+1

Blank = 21 ± 5 µg.

These results show that precision and accuracy, as good as

can be expected from spectrophotometric titrations can sometimes be obtained visually, and that the precision improves with practice. The first two results, however, suggest that a precision of ± 10 µg is more likely in odd paired experiments. A series of experiments with different amounts of zinc treated similarly gave irregular results:

Zinc taken, µg	2094	529	522	270	246
Zinc found, µg (corrected)	2099	541	491	254	240
Error, µg	+5	+12	-31*	-16	-6

Blank = 24 µg of zinc.

The result marked * was definitely associated with undertitration, but at the time it was thought that the end-point had been reached.

To compare the visual and spectrophotometric procedures from the stand-points of precision and accuracy, two series of experiments, all with 350 µg of zinc, were performed, one by each procedure. The initial solutions contained hydrochloric, hydriodic and nitric acids, and were treated as described above. The results obtained are shown below.

Visual Experiments:

Zinc taken, µg	345	363	369	377	374
Zinc found, µg (corrected)	369	401	391	401	392
Error, µg	+24	+38	+22	+24	+18

Blank = 4 ± 4 µg.

Spectrophotometric Experiments:

Zinc taken, µg	343	345	367	352
Zinc found, µg (corrected)	349	349	374	353
Error, µg	+6	+4	+7	+1

Blank = 31 ± 0 µg.

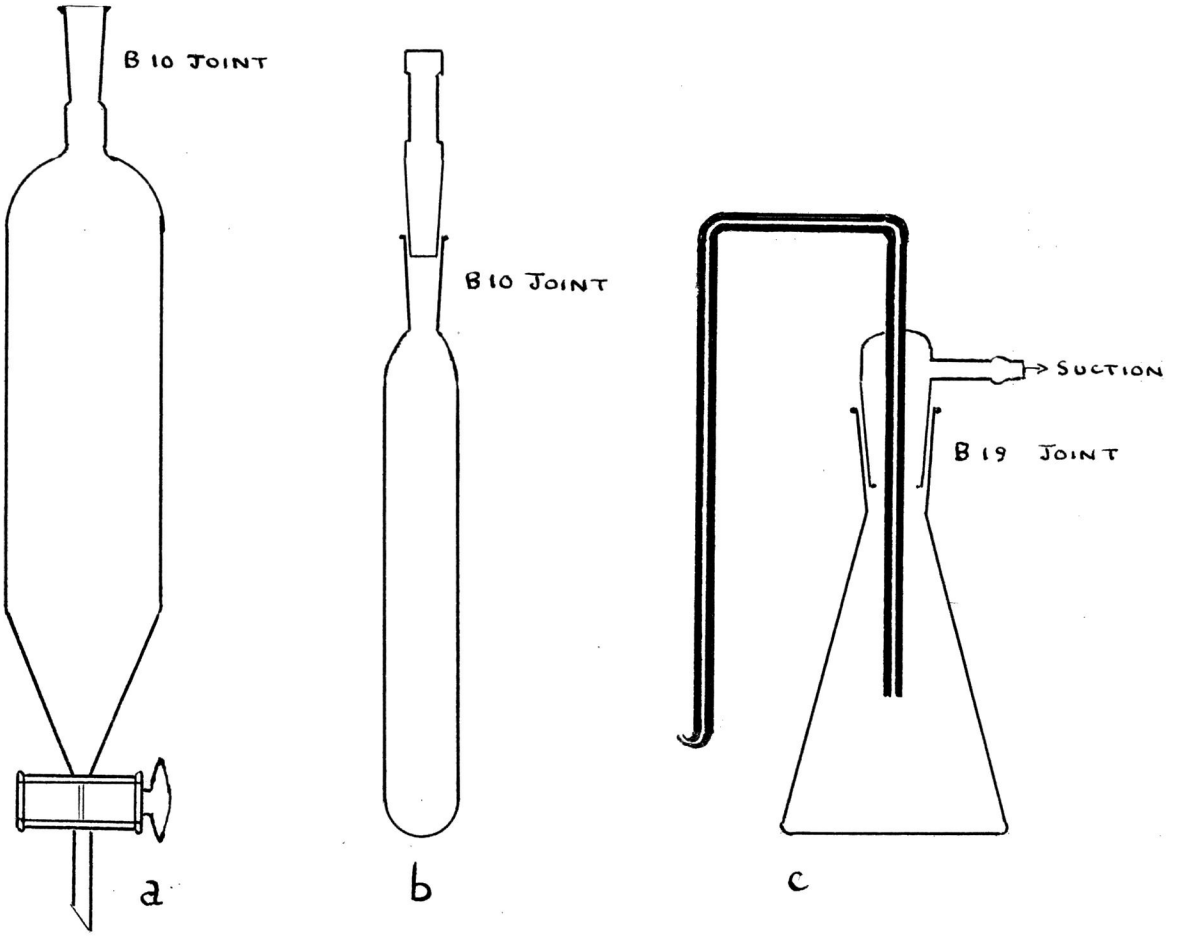
It is evident that the precision of the spectrophotometric set is somewhat better than for the visual set, and that the accuracy is considerably superior. The difference in accuracy is almost entirely due to the undertitration of the blank in the visual series, as if the other, presumably true, blank were used instead, the errors in the visual experiments would be -3, +11, -5, -3, -9 µg, respectively.

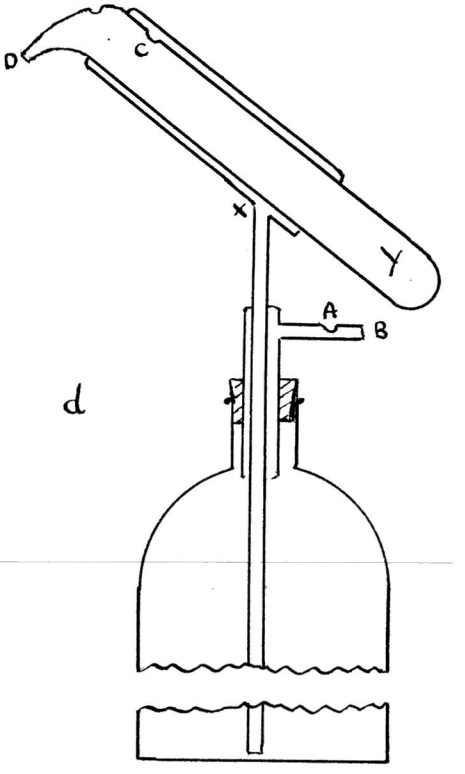
The visual titration procedure therefore gives results of reasonable precision, but there is liable to be a systematic error due to the use of a wrong value for the blank. With regard to titration in the presence of other elements, visual titration is unlikely to be satisfactory in presence of tin, and the 'triple titration' procedure recommended for lead and manganese cannot be used. Accurate direct titration of small amounts of manganese is difficult, and of lead impossible, because of slowness in the reactions. The solvent extraction procedure to be described is recommended in all cases where interfering elements (gallium, indium, lead, manganese, tin, titanium, and uranium) are present and visual titration has to be used, as with its aid all of these elements, except manganese, are eliminated. The small amount of manganese likely to be present in normal practice (>10 ug) can be neglected in visual work where the precision may be only 20 or 30 µg. Solvent extraction is also useful in visual titration experiments because the end-points are sharper than when it is not employed.

THE EXTRACTION OF ZINC PYRIDINE THIOCYANATE

In connection with the elimination of the interference due to iron^{III} and tin^{IV} in the determination of zinc by titration with disodium ethylenediaminetetra-acetate in ammonia-ammonium chloride buffered solutions of pH 10, with solochrome black as indicator, the possibility of solvent extraction of some zinc complex had been considered. Extraction of the zinc thiocyanate complex from acid solution as previously described (p. 16 et seq.) was tried, but while iron^{III} could be prevented from extracting by the addition of sufficient fluoride, tin^{IV} was extracted along with the zinc. The extraction of zinc pyridine thiocyanate was then investigated.

In the presence of thiocyanate, pyridine forms covalent complexes of low solubility in aqueous media with a number of bivalent ions, viz: Cd, Co, Cu, Fe, Mn, Ni, and Zn. The metal pyridine thiocyanates are all readily soluble in chloroform, and the possibility of extracting dithiocyanatodipyridinozinc with this or some other solvent as a means of separating zinc from iron^{III} and tin^{IV} was apparent. Spacu and Ripan (61) had extracted the zinc complex with chloroform in connection with a micro-gravimetric method for zinc, but no details of the conditions used are given in the abstract. Zinc also forms a complex with pyridine and iodide (122) which was found to be readily soluble in chloroform. Pyridine iodide complexes are formed with some other metals, including antimony^{III} and bismuth, whose complexes were found to be insoluble in chloroform. With lead, pyridine and thiocyanate precipitate Pb(OH)SCN (123), which is insoluble in chloroform, as is also the iodide complex. Of the metals





Operation of Semi-Automatic Pipette — Close A with finger and apply pressure at B. The liquid from the bottle rises in tube X and fills tube Y viâ C.

Release pressure at A by removing finger, allow to drain, and pour off liquid through D.

FIGURE 15

(HALF ACTUAL SIZE)

liable to accompany zinc in the eluates from anion-exchange columns (see Table XIV, p. 76), only copper^{II} and manganese^{II} would be expected to extract completely along with the zinc, with perhaps some iron^{II} which is apparently formed by reduction of iron^{III} by thiocyanate in neutral solution.

Conditions for the quantitative extraction of the zinc complex were initially worked out in conjunction with visual detection of the end-points in the titrations of zinc with ethylenediaminetetra-acetate, and the accuracy of the results, especially where sodium hydroxide was used for back-extraction of the zinc, is likely to be rather poor. It is believed, however, that the trends due to variations in the conditions were correctly determined. The method for eliminating the interference of iron^{III} by reduction with ascorbic acid and formation of ferrocyanide (cf. p. 87) is simpler than solvent extraction. The extraction technique is therefore now to be considered in relation to the separation of zinc from those other elements; gallium, indium, lead, tin^{IV}, titanium^{IV}, uranium^{VI}, which can still interfere in or complicate its determination with ethylenediaminetetra-acetate.

Selection of the Conditions for Extraction —— Most experiments were performed with specially constructed separating funnels and tubes - see Fig. 15.

Experiments with solid zinc pyridine thiocyanate, prepared by the method normally used for its quantitative determination (124), showed chloroform to be the best solvent of several which were tried. The substance was sparingly soluble in chlorobenzene, and essentially insoluble in iso-amyl alcohol, benzene, n-butyl acetate, methyl iso-butyl ketone, carbon tetra-

chloride, dichlorodiethyl ether, 2-ethyl-hexanol and triethyl citrate. Chloroform was therefore used in future experiments.

Preliminary experiments indicated that extraction was most nearly complete from solutions of pH just greater than 7, containing some free pyridine. If the pH were less than 6·5 or greater than 7·5 extraction was much less efficient, although some slight extraction occurred at pH 4. It was therefore essential that the chloroform used should contain no acidic or alkaline impurities, except perhaps traces of pyridine in recovered material. Tentative experiments on the extraction of 2-mg amounts of zinc from 60-ml volumes of chloride solutions treated with thiocyanate and pyridine, followed by addition of the chloroform extracts to ammonia-ammonium chloride buffers and titration with disodium ethylenediaminetetra-acetate, showed the method to be promising, although the presence of chloroform in the solutions for titration caused difficulty with the end-points. Methods for eliminating the chloroform were therefore examined.

As the chloroform solutions of the zinc pyridine thiocyanate were liable to be contaminated with grease from the stopcocks of the separating funnels in use, and also exhibited a tendency to creep over glass surfaces, evaporation of the chloroform was not likely to be a suitable technique for its elimination. Evaporation was used in a few experiments, especially where qualitative results were adequate, but was not considered safe for quantitative work. The possibility of using a back-extraction procedure was therefore examined. Qualitative experiments showed that the zinc complex could be readily broken down, and the zinc extracted, by either acid or alkali. Since with acid, the excess pyridine, which was extracted by the chloroform along with the zinc complex,

would be extracted and might later influence the buffering of the solution, extraction with alkali was preferred. Initially 10 ml of N-sodium hydroxide were used; later it was decided to incorporate cyanide; eventually, as a result of the finding in spectrophotometric titration experiments that sodium hydroxide, or some impurity associated therewith, was responsible for poor end-points, a change to the use of an ammoniacal cyanide solution was made.

A series of experiments was carried out in order to examine the effects of various concentrations of thiocyanate and pyridine on the extraction of zinc. The following procedure was used. The solution, containing *ca.* 2 mg of zinc, in 80 ml of ~0·15 N-hydrochloric acid, was neutralised (methyl red) with 2 N-sodium hydroxide, ammonium thiocyanate and pyridine were added, and then 10 ml of chloroform for extraction. The zinc was back-extracted with 10 ml of N-sodium hydroxide and the chloroform washed with three 5-ml portions of water. The sodium hydroxide extract and water washings were combined, buffered to pH 10 by the addition of ammonium chloride, and the zinc determined by titration with ethylenediaminetetra-acetate. The effects of various amounts of pyridine and thiocyanate are shown below.

Volume of 2 N-NH_4SCN, ml	0·25	0·25	0·25	0·5	1·0	2·0	5·0	1·0
Volume of pyridine, ml	0·5	1·0	1·5	1·0	1·0	1·0	1·0	1·0
Percentage of *ca.* 2 mg of zinc extracted	20*	45	45	55	80	95	95	80

* pH of extracted solution = 6·7. In all other experiments, pH was above 7.

The last result was obtained in an experiment where the initial solution contained hydrochloric, hydriodic and nitric acids as from a resin column, and was treated with thiosulphate

to reduce the free iodine before proceeding as above. The fact that the percentage extraction was the same as in the fifth experiment shows that iodide and nitrate are virtually without influence. In experiments where 2 ml of thiocyanate and 1 ml of pyridine were used, and 10 ml of chloroform for the extraction, followed by the addition of a further 0·5 ml of pyridine and extraction with a fresh 10-ml sample of chloroform, over 99 % of from 0·5 to 5 mg of zinc was apparently extracted from 80 ml of chloride solution. While these conditions showed considerable promise for the extraction of zinc alone, some modification might be necessary in the presence of other metals. Antimony^{III} and iron^{III}, for example, would be liable to precipitate as basic compounds unless a binding agent such as tartrate were present. Tartrate was found to decrease the percentage extraction of zinc, and the amount added had therefore to be controlled. With conditions such that a single extraction removed 95 % of the zinc in the absence of tartrate (2 ml of thiocyanate, 1 ml of pyridine), addition of 0·05, 0·2 and 0·5 g of tartaric acid before neutralisation lowered the extraction to 90 %, 75 %, and 50 %, respectively. Increasing the amount of thiocyanate counteracted the effect of tartrate, and in the final procedure the equivalent of 0·2 g of tartaric acid was employed in conjunction with 5 ml of 2 N-ammonium thiocyanate solution.

In many experiments, where two extractions had been given as described above, negative errors, generally about 60 µg irrespective of the amount of zinc taken (0·5, 2, or 5 mg) were found. It was considered that these were more probably associated with incompleteness of the initial extraction of the zinc pyridine thiocyanate by the chloroform than with faulty back-

extraction. The constancy of the error was suggestive of an adsorption effect, further indication of which was found in certain direct tests. One of these was conducted as follows. A solution was prepared for extraction and an aliquot removed and titrated. Some of the remaining solution was then stirred for a short time with coarsely powdered Pyrex glass, and a similar aliquot withdrawn and titrated. A smaller amount of zinc was found here. Loss of zinc occurred only in the presence of both thiocyanate and pyridine, suggesting that the zinc was being removed as the pyridine thiocyanate complex.

(The occurrence of adsorption of zinc from dilute alkaline solutions by glassware was reported at this time (125).)

Certain variations in the conditions for extraction, e.g. the addition of pyridine dissolved in chloroform, or cooling to 5°C, and the use of funnels coated internally with a silicone polymer or with oxygen cross-linked polyethylene, did not significantly improve the results. In experiments with polythene-coated funnels, it was necessary to extract with three 10-ml portions of chloroform, with the addition of 0·5 ml of pyridine after the first and second extractions, because the residual chloroform film on the walls was thick and irregular. For comparison purposes, a similar third extraction was given in an experiment with a non-coated funnel, and the zinc was found to be completely extracted. With this change to the use of three extractions, promising results were now obtained, the third extraction seemingly effecting the removal of the adsorbed material.

Some results for experiments, in which three extractions with 10 ml of chloroform (and additional pyridine) were given, are presented below. The initial neutralisation of the acid had

been effected with ammonia in order to minimise the value for the blank, and the back-extraction was performed with a solution containing 5 ml of 2 N-sodium hydroxide and 1 ml of 5 % w/v potassium cyanide solution in 10 ml. Buffering was achieved by the addition of 0·8 g of solid ammonium chloride before the titration. Bearing in mind the uncertainty likely to be associated with visual titrations with ethylenediaminetetra-acetate, especially with solutions containing sodium hydroxide, cyanide, and chloral hydrate, the results shown in Table XX indicate that the extraction technique is reasonably satisfactory.

TABLE XX

Zinc taken µg	Zinc found (corrected) µg	Error µg	Blank µg Zn
5987	5957	-30	55
5940	5927	-13	
5092	5074	-18	40
5048	5023	-25	
5061	5035	-26	40
4921	4905	-16	
483	502	+19	55
401	422	+21	

In all cases, including the blanks, the end-points were noticeably sharper than in titrations where treatment with cyanide and chloral hydrate had been applied to neutralised acid solutions, without extraction.

The use of ammonia for preliminary neutralisation of the acid was not found to influence the results in extraction experiments, although ammonium salts are stated to have a solvent

action on zinc pyridine thiocyanate precipitates (124).

Some tentative experiments by anion exchange - procedure 'C', p. 71 - followed by solvent extraction of zinc pyridine thiocyanate were performed with the following results:

Zinc taken, mg (approximate)	5	0·5
Error, µg (corrected for blank)	-19, -13	-14, -7, -18
Blank, µg of zinc	84	100

While these results show definite promise, the accuracy is not sufficiently good to be able to detect any slight interferences due to other elements initially present in conjunction with the zinc, when visual detection of the end-points in the titrations is employed.

With the development of procedures for spectrophotometric titration (p. 90 et seq.), the use of solvent extraction in conjunction with that technique was examined, especially as a means for separating zinc from interfering elements prior to titration. As it was desirable to avoid the use of sodium hydroxide in the preparation of the solutions for titration, an alternative back-extraction agent was required. Complete back-extraction was obtained with a mixture of 2 ml of 5 N-ammonium hydroxide, 1 ml of 5 % w/v potassium cyanide, 0·05 ml of 1 % w/v ascorbid acid and water to 10 ml. The ascorbic acid was added to prevent oxidation of bivalent iron or manganese which might be present. In order to ensure complete conversion of iron(II) to ferrocyanide, the back-extraction solution and washings were heated to *ca.* 75°C, and this heating was continued until any droplets of chloroform, which would otherwise attack the 'Perspex' titration cell, were removed. After cooling, the colour, on addition of solochrome black solution, was found to be orange,

indicating that the pH was too high. Addition of 1 ml of a 10 % w/v solution of ammonium chloride caused the development of the expected blue colour. In experiments with 5-mg amounts of zinc, it was found that the colour at this point was not pure blue unless a further 1 ml of 5 % w/v potassium cyanide solution were added, together with 1 ml of ammonium chloride solution. This effect is possibly due to a reaction, perhaps with the chloroform, causing removal of some of the cyanide. 2 ml of 50 % w/v chloral hydrate solution were used in such experiments. The full procedure for the extraction and back-extraction of zinc prior to spectrophotometric titration with ethylenediaminetetra-acetate is as follows.

Procedure for Solvent Extraction of Zinc Pyridine Thiocyanate —— For satisfactory separation of the phases, all apparatus must be thoroughly cleaned with chromic acid mixture and washed with distilled water before use. The minimum of grease for efficient lubrication of the stopcock of the separating funnel should be used.

To the solution, volume 60 - 80 ml, containing hydrochloric, nitric, and possibly hydriodic acids, contained in a suitable separating funnel (Fig. 15 a, p. 116*) add, if necessary, 1 % w/v ascorbic acid solution to decolorise iodine. If the solution has been collected from an anion-exchange column, as described on p. 131 , tartrate will already be present; otherwise add 1 ml of 25 % w/v ammonium tartrate solution. Add 5 N-ammonium hydroxide until the solution is barely alkaline to methyl red, followed by 5 ml of 2 N-ammonium thiocyanate solution. Mix by shaking the stoppered funnel, and then add 1 ml of pure pyridine and mix again. Add 10 ml of chloroform (a semi-automatic

pipette, cf. Fig. 15 d, may conveniently be used) and shake the mixture briskly for 1 minute (250 shakes). Allow to settle, swirling or swaying the funnel gently in order to sink any chloroform that collects at the air-water interface, and run off the chloroform into the back-extraction tube (Fig. 15 b), containing 2 ml of 5 N-ammonium hydroxide, 0·05 ml of 1 % w/v ascorbic acid and 2 ml of 5 % potassium cyanide, with water to make 10 ml. ⁂ To the contents of the separating funnel add 0·5 ml of pyridine, in such a manner as to wash the ground surface of the socket, and mix. A marked turbidity generally develops. Extract as before with 10 ml of chloroform, allow to separate, and run this off into the back-extraction tube. Repeat from ⁂. Rinse the stem of the funnel into the tube with 0·5 ml of chloroform.

Shake the back-extraction tube briskly for 1 minute, allow to settle, and withdraw the aqueous layer as completely as possible via a bent capillary with upward-pointing tip (Fig. 15 c), collecting the solution in a flask containing 2 ml of 10 % w/v ammonium chloride solution. Wash the chloroform remaining in the back-extraction tube with three 5-ml portions of water, shaking for about 30 seconds with each and treating as above. Discard the chloroform, or else save it for recovery (see p. 11).

Heat the solution on a hot-plate to ~75 °C for 10 minutes or until any droplets of chloroform have evaporated, cool in running water and add solochrome black solution (p. 93). If the colour is not blue, spectrophotometric titration with ethylenediaminetetra-acetate here is required, and may be performed directly, except for blanks, as with manganese in the small amounts likely to be present there is no serious slowness in the

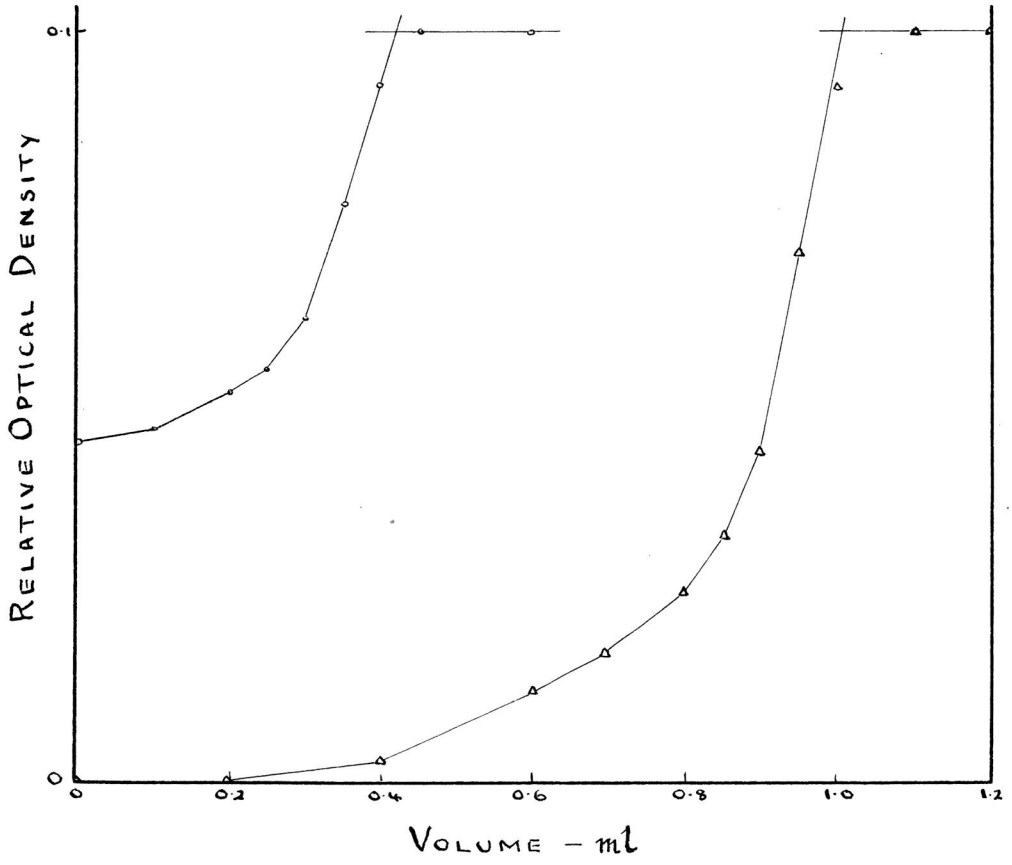


FIGURE 16

reaction, but see, however, p. 103. If the colour is blue, or after such preliminary titration, add 2 ml of 50 % w/v chloral hydrate solution and titrate the liberated zinc spectrophotometrically as previously described (p. 108). The end-point is sharper than for normal titrations in presence of cyanide and chloral hydrate, and should be approached very cautiously. A full extraction blank should be similarly performed and determined.

Some results for extraction experiments on different amounts of zinc are given in Table XXI. All solutions contained hydrochloric acid, hydriodic acid, and nitric acid as from a resin column before preparation for the extraction.

TABLE XXI

Zinc taken µg	Zinc found (corrected) µg	Error µg	Blank µg Zn
4937	4916	-21	35
4925	4908	-17	
1347	1351	+4	41
1329	1333	+4	
372	378	+6	25
344	352	+8	

Typical titration curves obtained in extraction experiments are shown in Fig. 16, which should be compared with Figs. 8 and 12 (pp. 93* and 97*, respectively).

THE USE OF THE EXTRACTION TECHNIQUE FOR THE SEPARATION OF ZINC FROM OTHER METALS

No detectable extraction from the stated amounts of the following metals was found to occur: gallium, 5mg; indium, 2·5 mg; titanium^{IV}, 2·5 mg; uranium^{VI}, 1 mg. With tin^{IV}, slight extraction (0·5 mg) was found to occur from 10 mg initially present, but

with the small amounts ($\leqslant$3 mg) likely to be present after the use of methylarsonic acid and anion exchange, no extraction was detected. Lead (~1 mg) formed a precipitate, which neither extracted nor impeded separation of the phases. In experiments with 1 - 2 mg of lead present, an unidentified impurity, equivalent to 20 μg of lead (or 6·5 μg of zinc), but unlike lead readily titrated at the cyanide stage with ethylenediaminetetraacetate, was apparently extracted. Its nature was never elucidated and for most purposes it was adequately dealt with by running a control experiment on the lead solution without added zinc, carrying this through the whole procedure as for a blank. 2·5 Mg of antimony^{III} or of bismuth yielded nothing to the extract. If treatment of the resin with hydriodic acid were omitted, any bismuth reaching the eluate along with the zinc would thus be eliminated by extraction and prevented from interfering in the titration. On extracting a solution to which ca. 10 mg of iron(III) had been added, 700 μg of iron(II) was found to go into the chloroform. No ascorbic acid was used in this experiment, so that thiocyanate must have been responsible for the reduction. Small amounts of copper and manganese were, as expected, essentially completely extracted. The amount of tartrate present in the recommended procedure (p. 123) is adequate for the prevention of the precipitation of the maximum probable amounts of the various other elements, except indium which precipitates as hydroxide even in the presence of tartrate.

The results given in Table XXII for experiments on the extraction of zinc from numerous combinations of the above-mentioned elements show that there is no important evidence of interference from them.

TABLE XXII

Zinc taken µg	Zinc found (corrected) µg	Error µg	Other Elements in mg
4975	4943	-32	In, 5; Pb, 2; Sn^{IV}, 5; Ti^{IV}, 2·5; U^{VI}, 0·25
4930	4910	-20	
444	435	-19	Pb, 2
432	429	-3	
355	344	-11	In, 5; Ti^{IV}, 2·5; U^{VI}, 1
342	331	-11	

The time required for solvent extraction, back-extraction, and a single titration is about 30 minutes, which is comparable with that required for a 'triple titration' (p. 111). Since it enables zinc to be determined in the presence of gallium, indium, titanium, and uranium, which cannot otherwise be satisfactorily dealt with, its use is recommended for samples of unknown composition, in which these other elements are likely to be present. Except for materials of very high manganese content, it should not be necessary to 'triple titrate' after a solvent-extraction separation has been carried out on the eluate from an anion-exchange column. It is conceivable that the techniques might be applicable directly to the determination of zinc in certain materials, such as aluminium or magnesium alloys, but this has not been investigated.

THE SEPARATION OF SMALL AMOUNTS OF ZINC FROM OTHER ELEMENTS BY ANION EXCHANGE IN RELATION TO ITS DETERMINATION WITH DISODIUM ETHYLENEDIAMINETETRA-ACETATE

Three procedures for the anion-exchange separation of zinc from other metals have been described (pp. 53, 66, and 71) The majority of the results which have so far been obtained by them relate to the gravimetric determination of zinc with 8-hydroxy-quinoline, and to amounts greater than 5 mg, although a few experiments with smaller quantities have given promising results. In view of the development of methods for the determination of from less than 0·5 to 5 mg of zinc by titration with disodium ethylenediaminetetra-acetate, the study of the adsorption and recovery of small amounts of zinc could now be undertaken more readily than was possible with the tedious micro-gravimetric procedure previously employed (p. 60). Some results for experiments with zinc alone have already been given in the discussion of the volumetric procedures for its determination (Tables XVII and XIX, pp. 89 and 99, respectively).

The behaviour of zinc in association with other elements was now thoroughly examined, the necessary determinations being performed by spectrophotometric titration. From experiments with many other elements (Table XIV, p. 76), those liable to accompany zinc on elution from anion-exchange columns had been determined, and various methods for preventing or avoiding interference from them have been described in the foregoing pages (pp. 99 - 106, 115 et seq.). Along with all experiments made with synthetic mixtures described hereafter, a control experiment was run as well as a blank. Such control experiments

were performed with all of the other constituents of the mixture except zinc, and were conducted in the same manner as blanks. They were carried out in order to correct for any zinc impurity in the solutions of the other elements used, but rarely did the amount of zinc found in the control differ from that found in the blank by more than a few micrograms, although the control was always used to calculate the results. In general, titration was carried out after treatment of the eluates with ascorbic acid, cyanide, and chloral hydrate, although where necessary other techniques, such as 'triple titration' or solvent extraction, were employed. In the experiment with zinc associated with cobalt, nickel and manganese, the amount of manganese accompanying the zinc was apparently nil, no necessity for titration at the cyanide stage being indicated. In confirmation of this, the control and blank experiments gave practically the same result, although both were titrated only after the addition of chloral hydrate. However, with a material, no control correction can be applied and titration at the cyanide stage should then be performed if manganese is suspected as being present. Solvent extraction was used in the experiments with large amounts of gallium, indium, and uranium, but not in the experiments with titanium and zirconium, where the amounts of titanium accompanying the zinc were apparently so small that rapid titration gave satisfactory end-points, nor in the experiments with tin and lead, where its use was not absolutely necessary.

The following outline procedure was employed.

Procedure for Anion-Exchange Separation of Small Amounts of Zinc

Prepare a resin column, apply to it the solution of zinc and other elements and wash with 2 N-hydrochloric acid as described on p. 53,

TABLE XXIII

DETERMINATION OF ZINC BY SPECTROPHOTOMETRIC TITRATION WITH DISODIUM ETHYLENEDIAMINETETRA-ACETATE AFTER ANION-EXCHANGE SEPARATIONS OF MIXTURES

Zinc taken (approx.)	Other Elements or radicals		Separation Procedure	Error	Zinc taken (approx)	Other Elements or radicals		Separation Procedure	Error
mg		mg	*	µg	mg		mg	*	µg
0·6	Cu	100	A	+1, +5	0·4	Al	100	B	-8, +3
5 0·4	Cd	100	B	+10, +5 -5, +7	0·4	Co^{II}, Ni, Mn^{II} 1: 2: 2	100	A	+1
0·4	Fe^{III}	100	B	+13, +8	5 0·5	Pb†	(100)	B	+26, +36 -3, 0
5 0·3	Sn^{IV}	100	C	-31, +7 -11, -3	5 0·4	Bi	50	B	-2, +4 -7, -8
5 0·4	Sb^{III}	50	B	+13, +8 -7, -9	5 0·4	Sb^{V}	50	B	+11, +6 -9, +5
0·5	Be	5 100	A	+6 +3	0·5	Cr^{III}	5 100	A	+3 +7
0·5	Ti^{IV}	5	A	-9	0·5	Zr	5	A	-10
0·5	Ti^{IV}, Zr 1: 1	100	A	+7, +5	0·5	Th	5 100	A	+3 +2
0·4	Ga	100	AX	+3, -1					
0·5	In	100	AX	-4, -8	0·5	U^{VI}	5 100	A AX	+7 -7, -5
5 0·4	$SO_4^{=}$	250	A	+20 +21	0·4	Au^{III} Pt^{IV} Tl^{III} Hg^{II}	25 each	B	-24, -9
5 0·4	$PO_4^{\equiv}$	50	A	+8 (-22), -3, C	5 0·4	$AsO_4^{\equiv}$	50	A	+3 -6
5 0·6	$AsO_3^{=}$	50	A	-1 +1	5 0·5	NO_3^{-} ClO_4^{-}	50 each	A	-3 +6

* A = elution with water and nitric acid, cf. p. 53

B = elution with hydriodic acid, water and nitric acid, cf. p. 66

C = methylarsonic acid procedure, cf. p. 71

X = solvent extraction of zinc pyridine thiocyanate, cf. p. 123.

† Most lead removed as chloride at start.

or if tin is present and the methylarsonic acid procedure is to be employed, proceed as on p. 71. Elute the zinc by the appropriate method (pp. 53, 66), collecting it in a flask containing 1 ml of 25 % w/v ammonium tartrate solution, or if solvent extraction of zinc pyridine thiocyanate is to be used, directly in the separating funnel (Fig. 15 a, p. 116*) containing this amount of tartrate. Proceed with the appropriate titration as described on pp.108 and 110, or with the solvent extraction as described on p. 123. Carry out a blank through the entire procedure, and, in addition, if a synthetic mixture is being examined, a control experiment with the components other than zinc. Resin from which the zinc has been eluted by means of water and nitric acid may sometimes be regenerated (see p. 55), but iodide-treated resin should be rejected after use.

The results for a large number of experiments with various synthetic mixtures are given in Table XXIII. Further comment is required in the following cases only.

In the experiment with 5 mg of uranium and 0·5 mg of zinc, an end-point was obtained on titrating rapidly, but on standing the titrated solution became pink, due to blocking of the indicator.

A duplicate of the experiment with cobalt, nickel, and manganese gave no end-point, probably due to accidental catalytic oxidation of the indicator by manganese(III), as the colour rapidly became yellow.

The results for the experiments with 5 mg of zinc in association with lead may be compared with those for check 'triple titration' experiments given on p. 103, where a similar positive error was encountered.

The large amount of sulphate examined (250 mg) was used in view of the possible application of a bisulphate fusion as a preliminary step for determining zinc in, say, a siliceous material after treatment with hydrofluoric acid.

It is seen that results of good precision and accuracy are obtained for the determination of zinc separated from other elements and radicals by the procedures described. For the 44 experiments with ca. 0·5 mg of zinc, the mean error is -1 µg and the standard deviation is 8 µg, whereas for the 17 experiments with ca. 5 mg of zinc, the corresponding figures are +7 µg and 16 µg respectively. Most of these results are for the determination of zinc originally associated with other elements which are either completely adsorbed by the resin or partially eluted along with the zinc, i.e., for the more troublesome combinations. Many of the experiments relate to amounts of the other elements very much greater than would be encountered in common zinc-containing materials. It is obvious that the method has a wide range of applicability.

The blanks were commonly of the order of 50 µg of zinc whichever ion-exchange procedure was employed, and this is probably about the lower limit to the amount of zinc which may be accurately determined. In a general way, for the determination of from ca. 0·05 to 5 % of zinc in a material of unknown composition, ion-exchange by procedure 'B' (p. 60) followed by solvent extraction of zinc pyridine thiocyanate and spectrophotometric titration with ethylenediaminetetra-acetate may be expected to give satisfactory results. In certain cases, solvent extraction might be omitted and 'triple titration' used instead.

ANALYSES OF MATERIALS

In view of the satisfactory results obtained for the determination of small amounts of zinc in synthetic mixtures, a number of different materials containing similar quantities of zinc were analysed by the methods described above. 100-mg samples of the alloys were dissolved with hydrochloric acid and the minimum of perhydrol, the solutions evaporated to dryness and the residues taken up in 5 ml of 2·0 N-hydrochloric acid. After heating to extract lead chloride, cooling and separating it if necessary (cf. p. 57), the solutions were applied to the resin columns and treated as previously described. With the bronze and the aluminium alloy '181', one experiment by each procedure 'B' and 'C' was performed. With the other aluminium alloy, both experiments were by procedure 'B'. White Metal 'A' (high in lead) was treated by procedure 'B' and White Metal 'B' (high in tin) by procedure 'C'. 'Triple titration' was used in all cases, because of the presence of lead.

For the analysis of the borosilicate glass, treatment with hydrofluoric and sulphuric acids was not used as the barium sulphate precipitate which would then form might be objectionable. Instead, hydrofluoric and perchloric acids were used, and much difficulty was experienced in early experiments due to 'spitting' caused by the sudden evolution of boron trifluoride during the early stages of the decomposition. The procedure is given in detail as being probably applicable to other similar materials.

Procedure for decomposition of borosilicate glass —— To the sample (100 mg) in a 6-ml platinum crucible, add 0·15 ml of water and 0·5 ml of 40 % hydrofluoric acid and stir with a platinum wire. After a few minutes, place on platinum foil on a hot-plate

TABLE XXIV

DETERMINATION OF ZINC IN MATERIALS

Material	Approximate composition									Zinc in material by certificate			Zinc found
	Cu %	Sn %	Fe %	Pb %	Al %	Sb %	Mn %	Mg %	Ni %	Min. value %	Max. value %	Average value %	%
Bronze No. 183	85	10	0·1	2	-	<1	-	-	-	1·72	2·00	1·86*	1·88‡, 1·89‡
Aluminium alloy No. 181	5	≪1	0·5	2	87	-	-	1	2	2·16	2·54	2·37*	2·41‡, 2·42‡
Aluminium alloy	2	6	0·6	1	89	-	-	-	-	-	-	0·80§	0·94‡, 0·94‡
White Metal 'A', No. 177	<1	5	0·1	83	-	12	-	-	-	0·02	0·16	0·08*	0·03‡, 0·03‡
White Metal 'B', No. 178	4	84	≪1	4	-	8	-	-	-	0·31	0·47	0·40*	0·44‡, 0·44‡
	SiO_2 %	BaO %	$Al_2O_3+Fe_2O_3$ %	CaO %	Na_2O %	K_2O %	B_2O_3 %	F %					
Sealing Glass, Sample No. 16391	65	3	5	1	6	3	15	<1		-	-	1·86/	1·89‡, 1·87‡

* British Chemical Standard certificate values.

‡ Ion exchange by procedure 'B', p. 66.

‡ Ion exchange by procedure 'C', p. 71.

§ Result of spectrographic analysis by J.J.M.Campbell.

/ Value supplied by General Electric Company, Limited.

of surface temperature ca. 100°C and evaporate to dryness in an air current, stirring occasionally to ensure even evaporation. Add 0·1 ml of water, 0·25 ml of 40 % hydrofluoric acid, and 0·1 ml of 60 % perchloric acid, and evaporate as before, finally increasing the temperature of the hot-plate very gradually until all the perchloric acid is expelled. Add 0·2 ml of 60 % perchloric acid and heat to expel it. Dissolve the residue in 5 ml of 2·0 N-hydrochloric acid, apply the solution to a resin column, and proceed as previously described.

As the composition of the glass was at the time unknown, except for the presence of barium, the ion-exchange procedure 'B' (p. 66) was used followed by titration of the zinc in a solution which had been treated with cyanide and chloral hydrate.

The results for the various determinations are presented in Table XXIV. Those obtained for the British Chemical Standard materials are seen in all cases to be within the range of the certificate values. The precision, 0·01 % of zinc, is good throughout. The amount of zinc in White Metal 'A' is below the expected minimum limit for accurate determination (p. 132) and as the recovery of such small amounts has not been examined otherwise, these experiments must be regarded as tentative.

CONCLUSION

Three procedures for the anion-exchange separation of zinc from other elements, together with the use of 8-hydroxyquinoline or disodium ethylenediaminetetra-acetate have enabled the determination of zinc in a wide variety of synthetic mixtures and materials to be accomplished. The results obtained have generally shown moderate or good precision, and in view of the large number of other elements which have been considered in conjunction with zinc, it is felt that the determination of from 0·5 to 50 mg of zinc in 100 - 150 mg samples of a comprehensive range of materials should be possible without significant modification of the technique. The smallest amount of zinc which can reasonably be expected to be accurately determined is 50 μg, but the actual recovery of such small amounts has not been examined in detail.

Of the other techniques which have been examined, the two solvent extraction procedures, namely extraction of zinc thiocyanate with n-butyl acetate and the extraction of dithiocyanatodipyridinozinc with chloroform might be directly applicable to certain materials, but the anion-exchange separation, used in conjunction with the latter solvent extraction separation where necessary, is much more widely applicable. For the subsequent determination of the zinc, the volumetric method with disodium ethylenediaminetetra-acetate is both quicker and more generally applicable than the gravimetric method with 8-hydroxyquinoline, as with it provision can be made for masking or allowing for small amounts of some metals not previously eliminated. In view of the precision of the results obtained for the determination of 5-mg amounts of zinc by the volumetric technique (2 parts per 1000), it is to be expected that a similar precision for the

determination of larger amounts could be attained. This is better than that obtained with 8-hydroxyquinoline. Visual titration with a more concentrated ethylenediaminetetra-acetate solution might be used, or, alternatively, an aliquot containing *ca.* 5 mg of zinc could be removed and titrated spectrophotometrically.

These techniques for the determination of zinc might, of course, be used in conjunction with other separation processes after the necessary adaptations had been worked out, but such are the simplicity and effectiveness of the anion-exchange separation that it has much to recommend it. It is thought unlikely that any difficulty would be encountered in adapting the method to the micro-scale, perhaps with columns as in Fig. 2, p. 24. A method for the determination of cadmium as well as zinc could probably be devised, with anion exchange from 2 *N*-hydrochloric acid solution as the preliminary separation technique for removing many other elements.

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